Are lithium batteries viable for extreme environments ?

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Outline

– Advanced secondary batteries: operating temperatures and achieved performances
– The lithium-ion battery: thermodynamics and kinetics of self-discharge
– The components issues: anode, cathode, electrolyte, separator and sealing technologies
– What is needed for extreme environments
– Li/CF_x primary batteries
– Conclusion

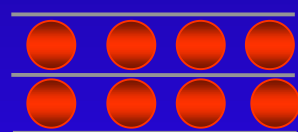
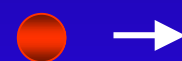
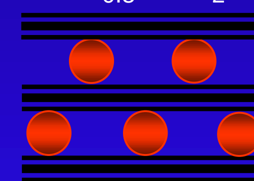
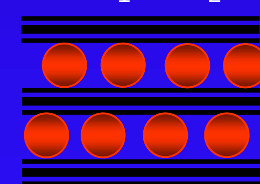
Advanced secondary batteries: operating temperatures and achieved performances

TABLE 37.7 Comparative Background Data for Rechargeable Battery Technologies[e]

Technology	Open-circuit voltage, V	Approx. closed-circuit, voltage,[a] V	Theoretical specific capacity,[b] Ah/kg	Theoretical specific energy,[b] Wh/kg	Operating temperature, °C	Recharge time, h	Self-discharge, % per month @ 20°C
Lead-acid	2.1	1.98	120	252	−20–50	8–24	3
Nickel-cadmium	1.35	1.20	181	244	−40–60	1–16	10
Nickel-iron	1.4	1.20	224	314	−10–60	5	25
Nickel-hydrogen	1.5	1.20	289	434	−10–30	1–24	60
Nickel-metal hydride	1.35	1.20	178	240	−30–65	1–2	30
Nickel-zinc	1.73	1.60	215	372	−20–50	8	15
Zinc/silver oxide	1.85	1.55	283	524	−20–60	8–18	5
Zinc/bromine	1.83	1.60	238	429	10–50	–	12–15[c]
Regenesys (polysulfide/bromine)	1.5	1.2	27	41	10–50	8–12	5–10
Vanadium-redox	1.4	1.25	21	29	10–50	6–10	5–10
Zinc/air	1.6	1.1	825[d]	1320[e]	0–45	–	–
Aluminum/air	2.73	1.4	2980[d]	8135[e]	10–60	–	–
Iron/air	1.3	1.0	960[d]	1250[c]	−20–45		15
Sodium/sulfur	2.08	2.0	375	755	300–350	5–6	–
Sodium/nickel chloride	2.58	2.47	305	787	250–350	3–6	–
Lithium-aluminum/iron monosulfide	1.33	1.30	345	459	375–500	5–8	–
Lithium-aluminum/iron disulfide	1.73	1.73	285	490	375–450	5–8	–
Li-C/$LiCoO_2$	3–4	3–4	100	360	−20–60	–	–
Li-C/$LiNi_{1-x}Co_xO_2$	3–4	3–4	–	–	−20–45	2.5	<3.5
Li-C/$LiMn_2O_4$-polymer elect.	3–4	3–4	105	400	−20–60	3	<2.5

[a] At $C/5$ rate.
[b] Calculated values based on the electrochemical cell reactions and the mass of active material.
[c] Finite self-discharge. This value applies if electrolyte is not circulating. Self-discharge is limited to that due to the amount of bromine in the cell stacks.
[d] Based on metal negative electrode only.
[e] See Ref. 10.

The lithium-ion battery: thermodynamics and kinetics of self-discharge

"normal operation"	Anode	Electrolyte	Cathode
DISCHARGE	LiC_6 		$Li_{0.5}CoO_2$ 
Theo. Capacity	372 mAh/g		138 mAh/g
CHARGE	Li_0C_6 		Li_1CoO_2 

The lithium-ion battery: thermodynamics

The chemistry of Li-ion batteries:

(-) graphite/organic liquid electrolyte/LiTMO (+)

(-) "Anode": $6C + xLi^+ + xe^- = Li_xC_6$ E^-
(+) "Cathode" $LiTMO = xLi^+ + xe^- + Li_{1-x}TMO$ E^+

(TMO= MO_2, M= Co, Ni, Mn…) or spinel Mn_2O_4)

OCV (cell) (x, T)= E^+(x, T) - E^-(x,T)

$\Delta G = \Delta H - T\Delta S = -nFE$

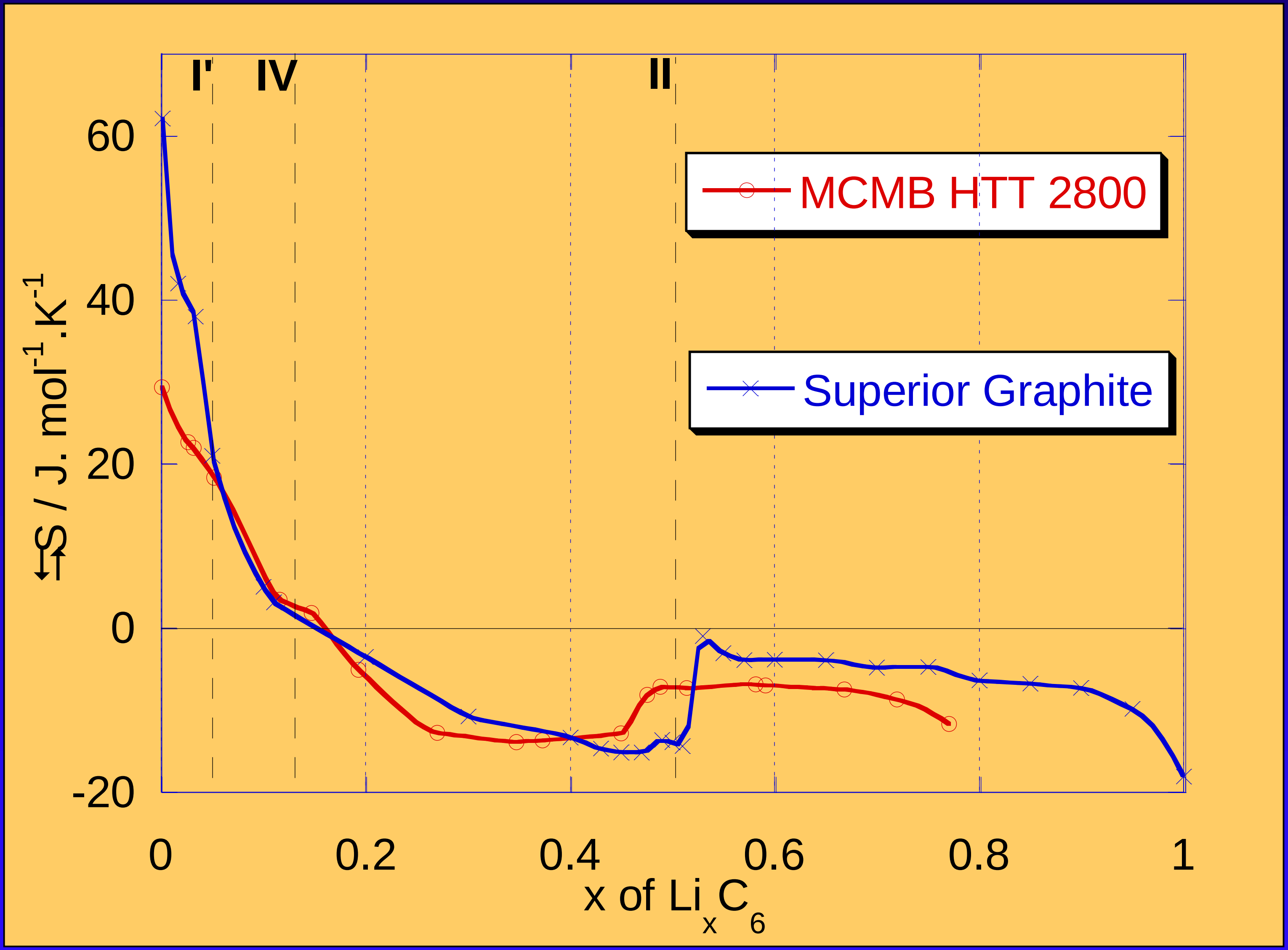
The lithium-ion battery: thermodynamics

$\Delta G = \Delta H - T\Delta S = -nFE$

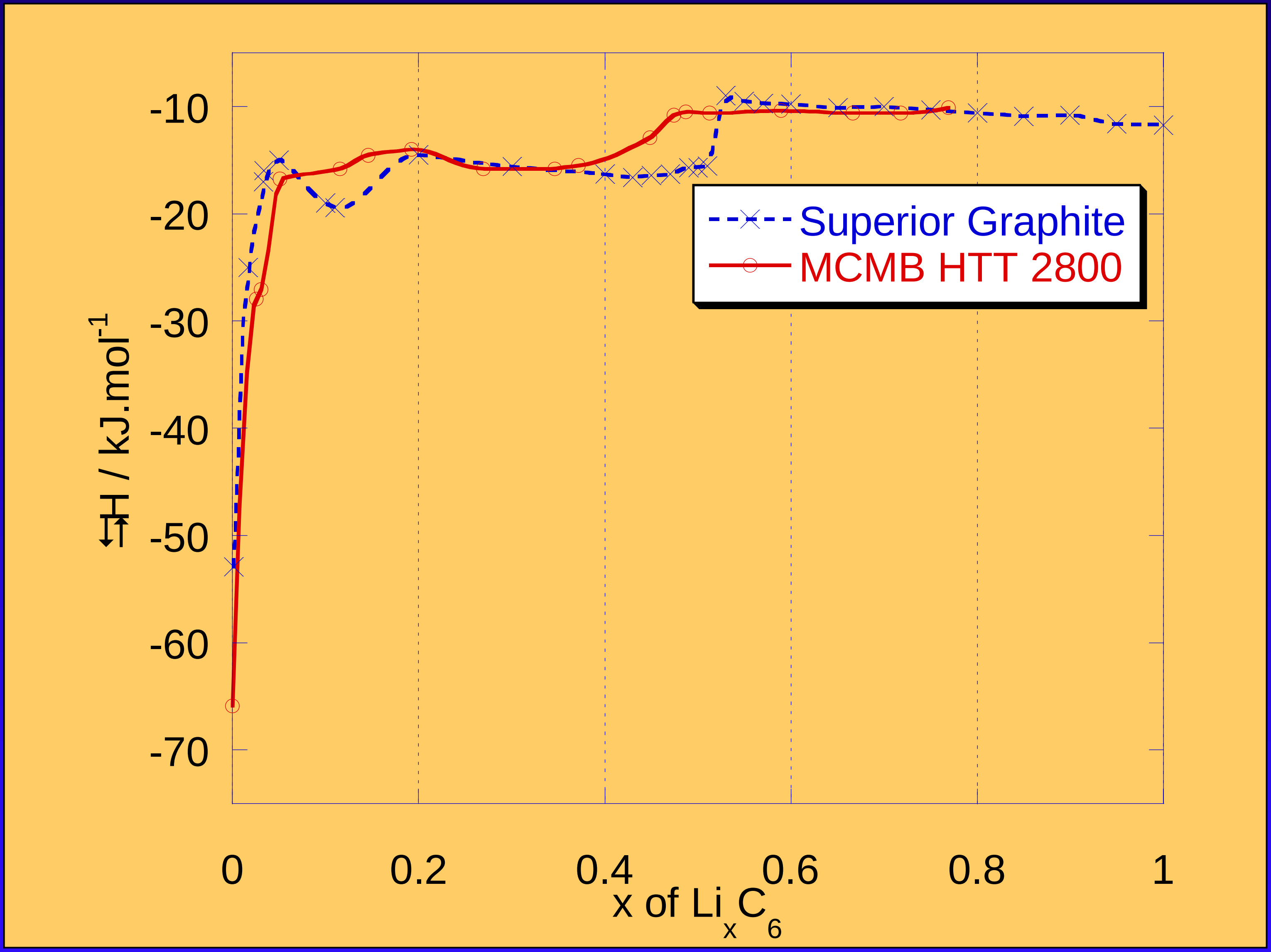
$\Delta S = F(dE/dT)_x$

$\Delta H = -FE + TF(dE/dT)_x$

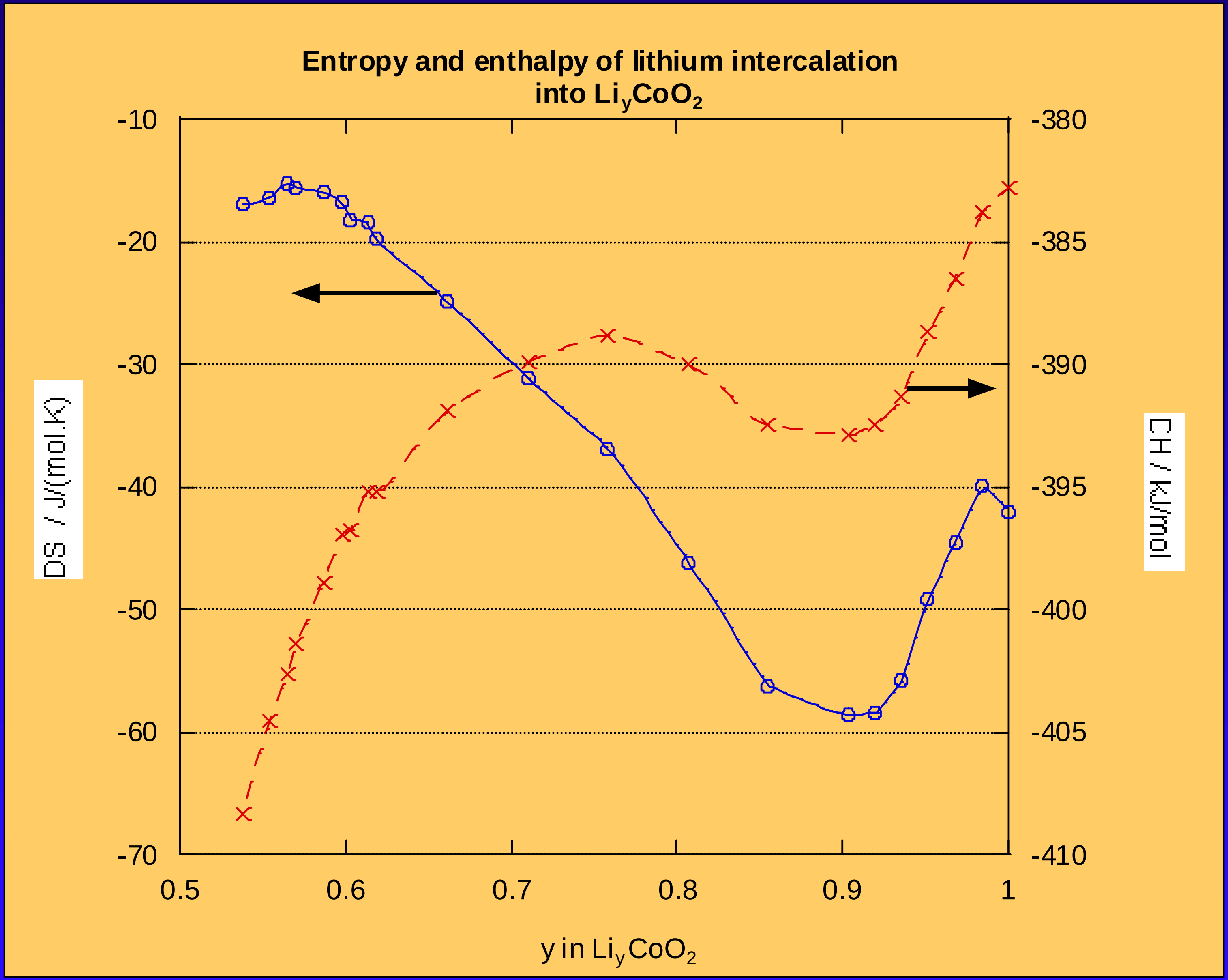
Thermodynamics: anode



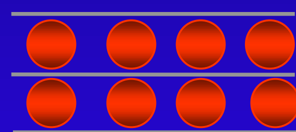
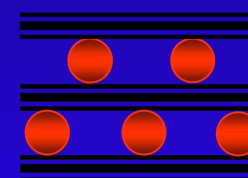
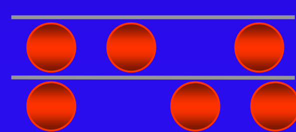
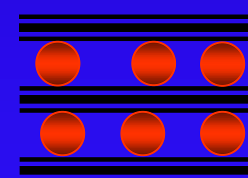
Thermodynamics: anode



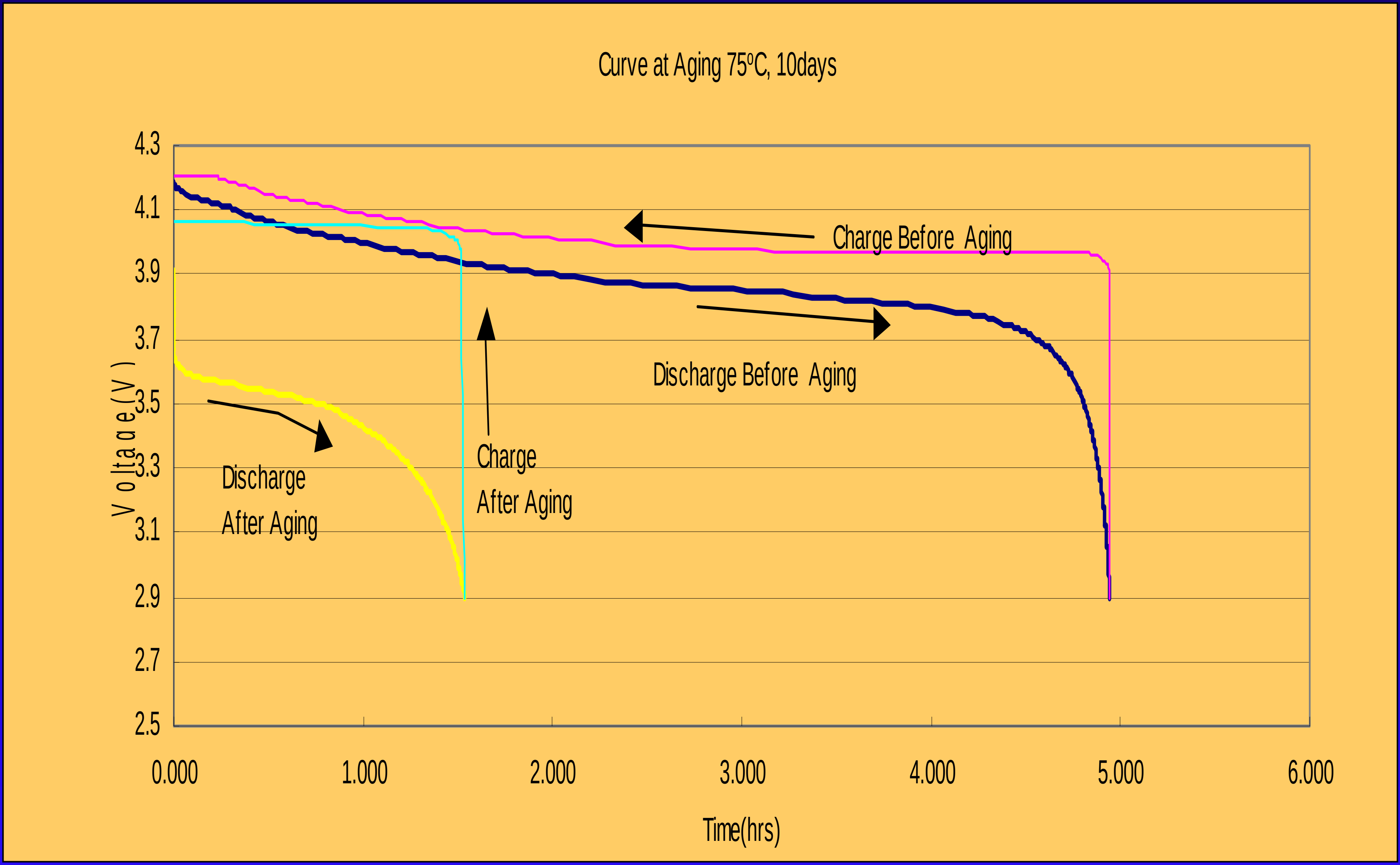
Thermodynamics: Cathode



principle of self-discharge

self-discharge	Anode		Cathode
Before	LiC_6 	(ideally) $372.m_{an}=138.m_{ca}$	$Li_{0.5}CoO_2$ 
Capacity loss (mAh)	**$372.m_{an}.x$**		**$138.m_{ca}.y$**
After	$Li_{1-x}C_6$ 	Lowest of $372.m_{an}.(1-x)$ and $138.m_{ca}.(1-y)$	$Li_{0.5+y}CoO_2$ 

Aging Effect (Cathodes)



Principle of self-discharge (III)

Measurements

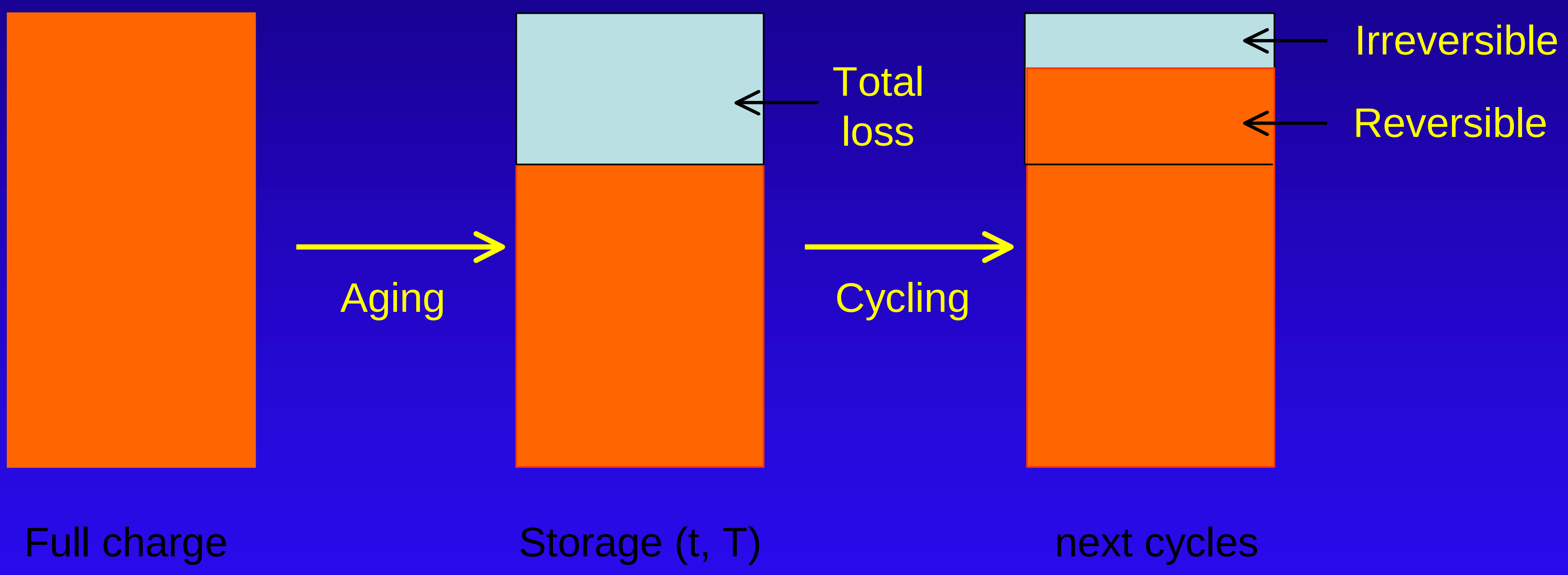
- *The capacity loss:*

  Is measured as the difference between the <u>discharge</u> capacity before and after storage:

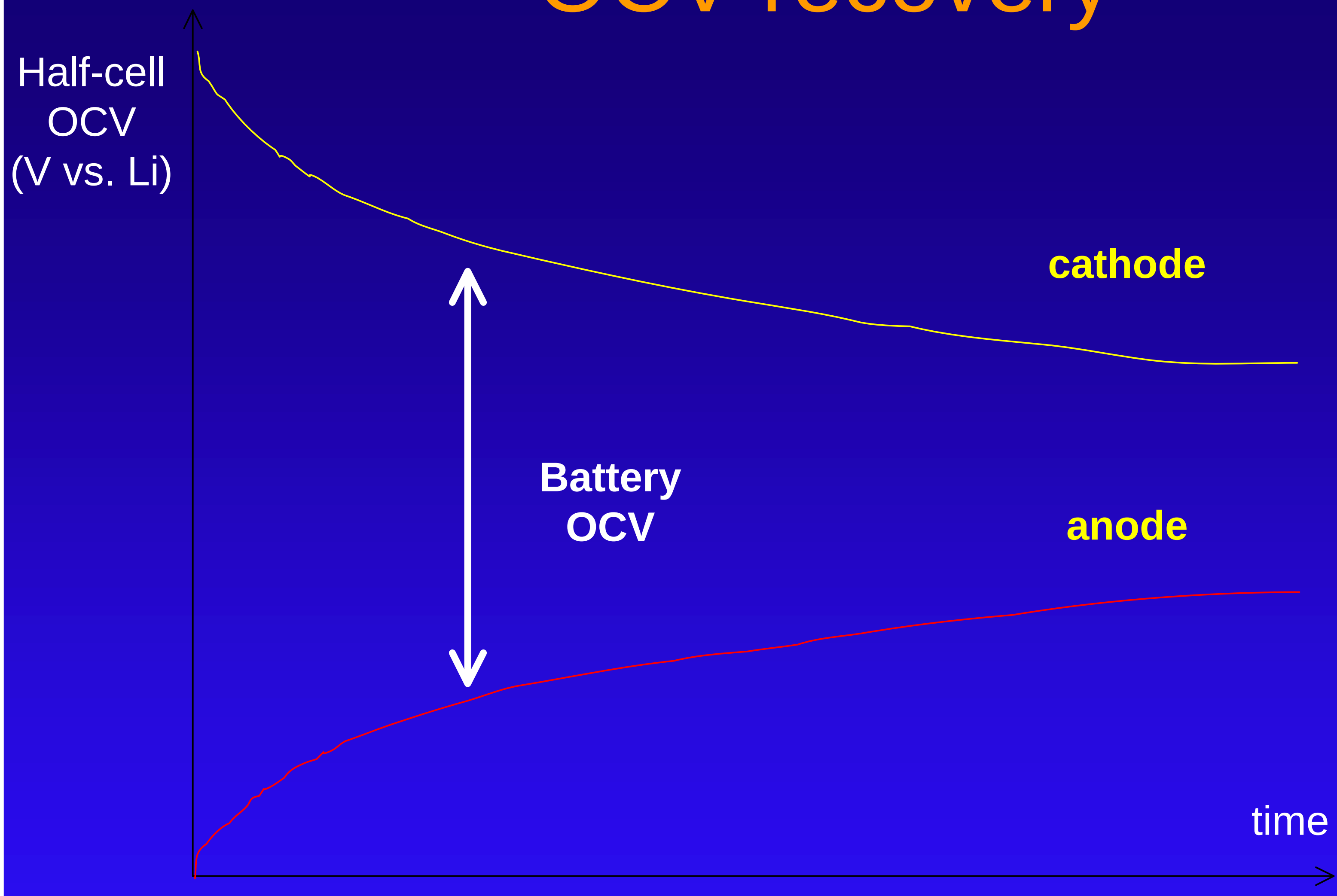
  - Anode: Li-deintercalation (charge of a Li/Li_xC_6 half-cell)
  - Cathode: Li-intercalation (discharge of a Li/$Li_{0.5+y}CoO_2$ half-cell)

- *OCV vs. time curve:*
  - Anode: OCV $\nearrow$: μ_{Li}(interface) $\searrow$
  - Cathode: OCV $\searrow$: μ_{Li}(interface) $\nearrow$

Reversible & irreversible capacity losses



OCV recovery



Objective of this work

– find the kinetics laws that govern:
  - OCV = f(t,T)
  - Capacity loss =f(t,T)
- – mechanism of the total capacity loss
- – origin of the irreversible capacity loss

-2016 coin cell-type were used:

Li / LiPF6 ,1M in EC(1):DMC(1) / Graphite (SG, USA)
Li / LiClO4,1M in PC / LiCoO2 (Enax. Japan)

- After 5 cycles @ C/5-rate at ambient temperature, the cells were stored at initial voltage:

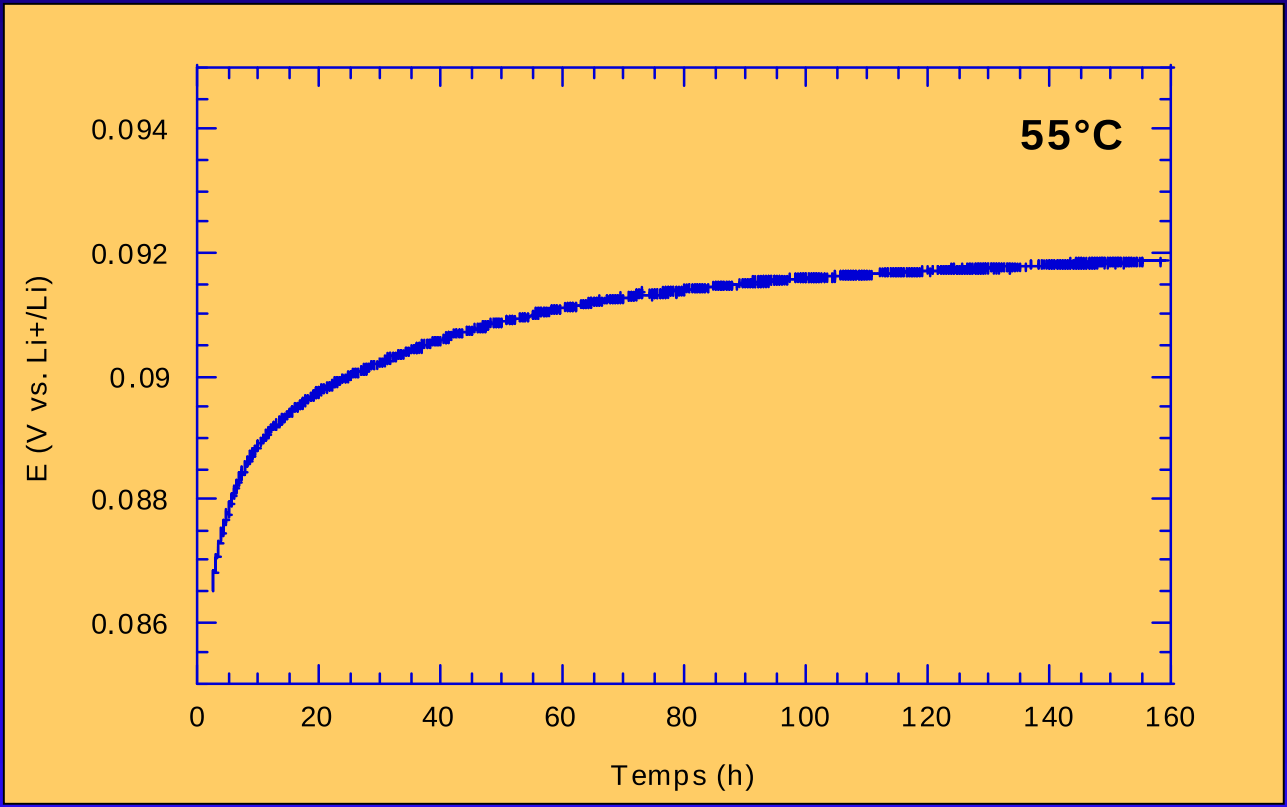
0 V for the anode (lithiated state: LiC_6)
4.2 V for the cathode (delithiated state $Li_{0.5}CoO_2$)

between 50 C < T < 75 C for periods up to 4 weeks

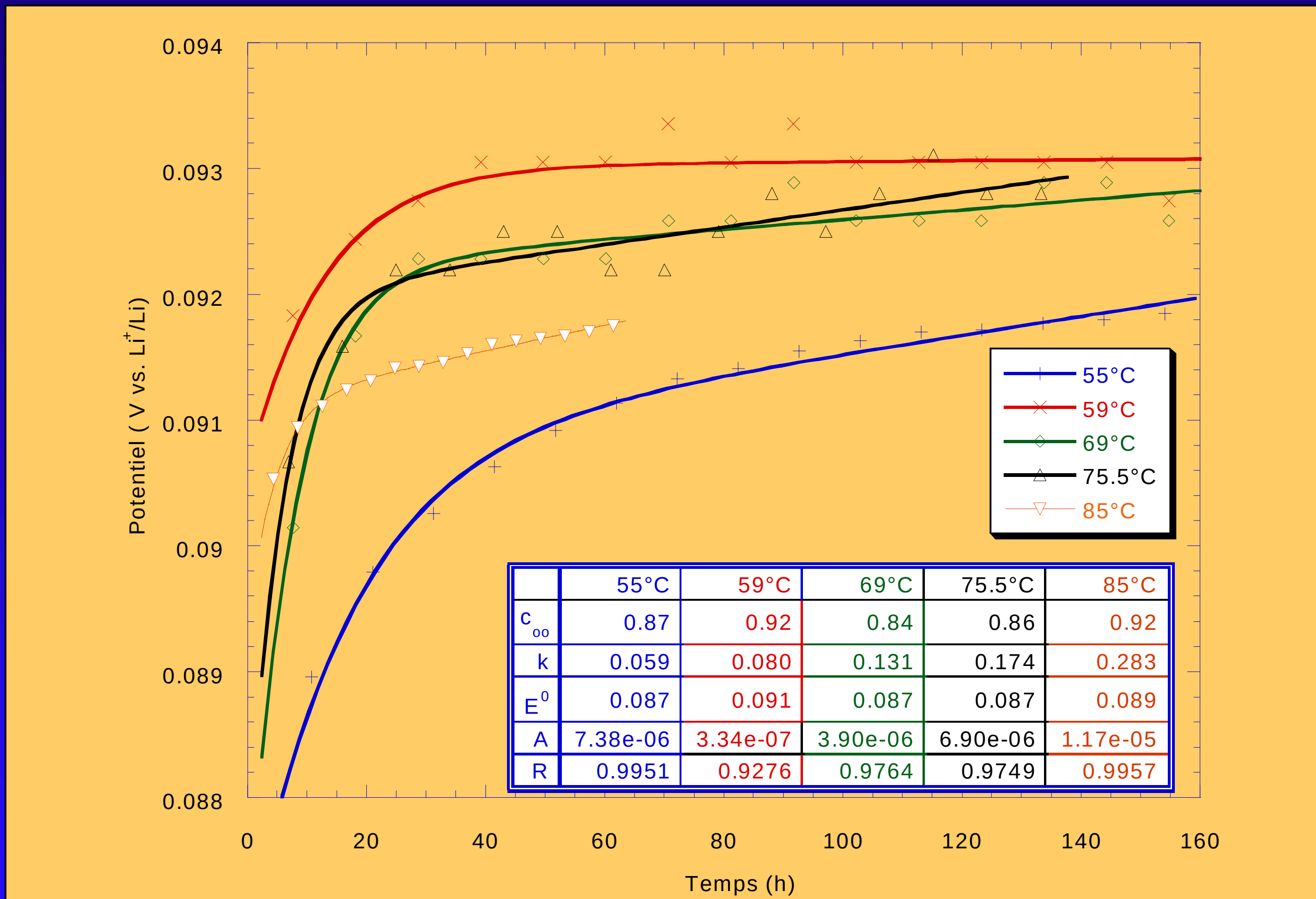
- OCV was monitored during aging at T
- The cells were then charged (anodes) or discharged (cathodes) and cycled for several cycles at ambient temperature

OCV measurements

– **Anodes:**



OCV measurements (anodes)



	55°C	59°C	69°C	75.5°C	85°C
c_{oo}	0.87	0.92	0.84	0.86	0.92
k	0.059	0.080	0.131	0.174	0.283
E^0	0.087	0.091	0.087	0.087	0.089
A	7.38e-06	3.34e-07	3.90e-06	6.90e-06	1.17e-05
R	0.9951	0.9276	0.9764	0.9749	0.9957

OCV measurements (anodes)

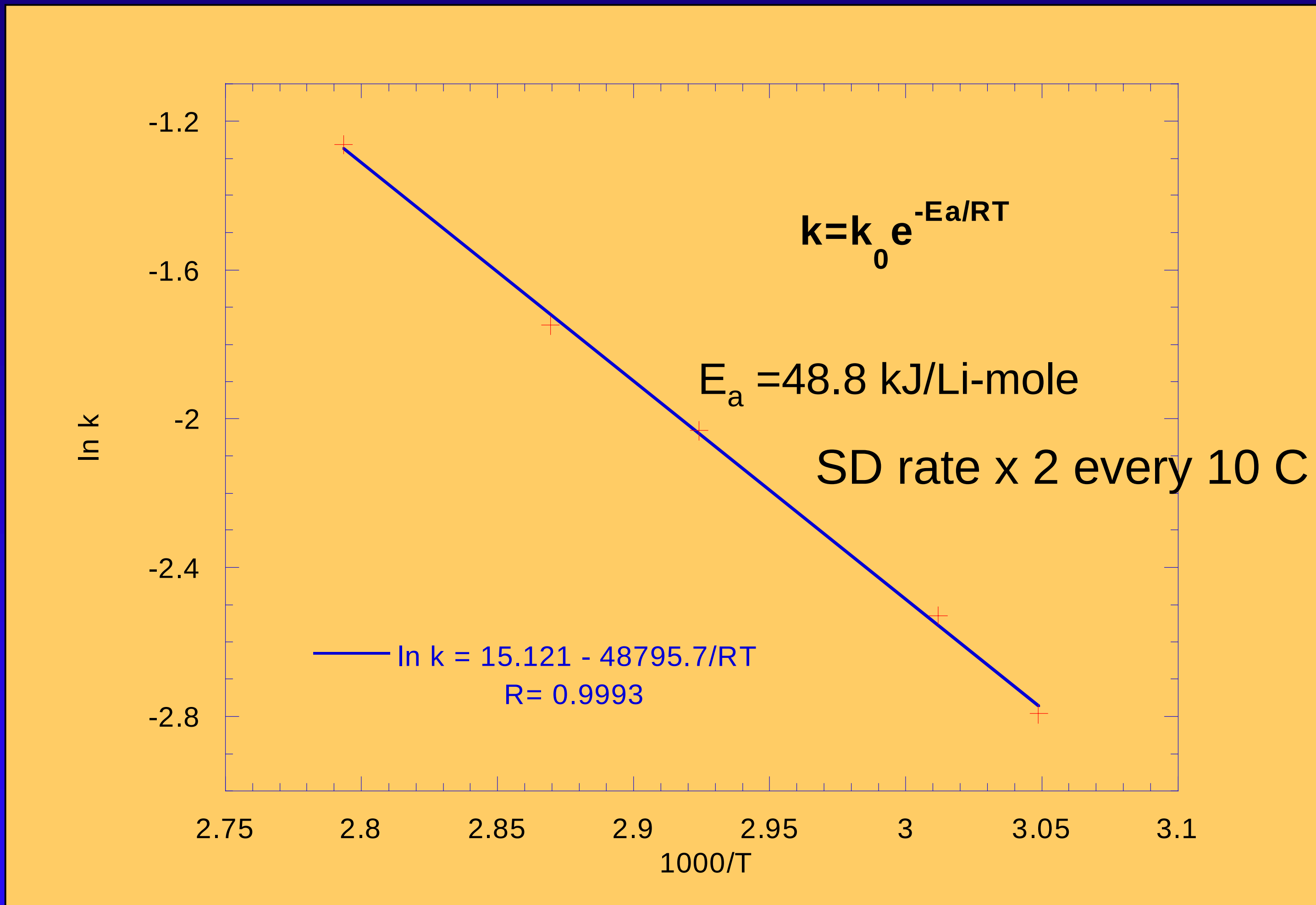
$$\begin{cases} LiC_6 \rightarrow Li_{1-x}C_6 + xLi_{ads} \\ Li_{ads} + nOx \leftrightarrow \left(Li^+, nOx, e^-\right)_{ads} \rightarrow LiM \end{cases}$$

$$v = k'[Li_{ads}].[Ox]^n = -\frac{d[Li_{ads}]}{dt}$$

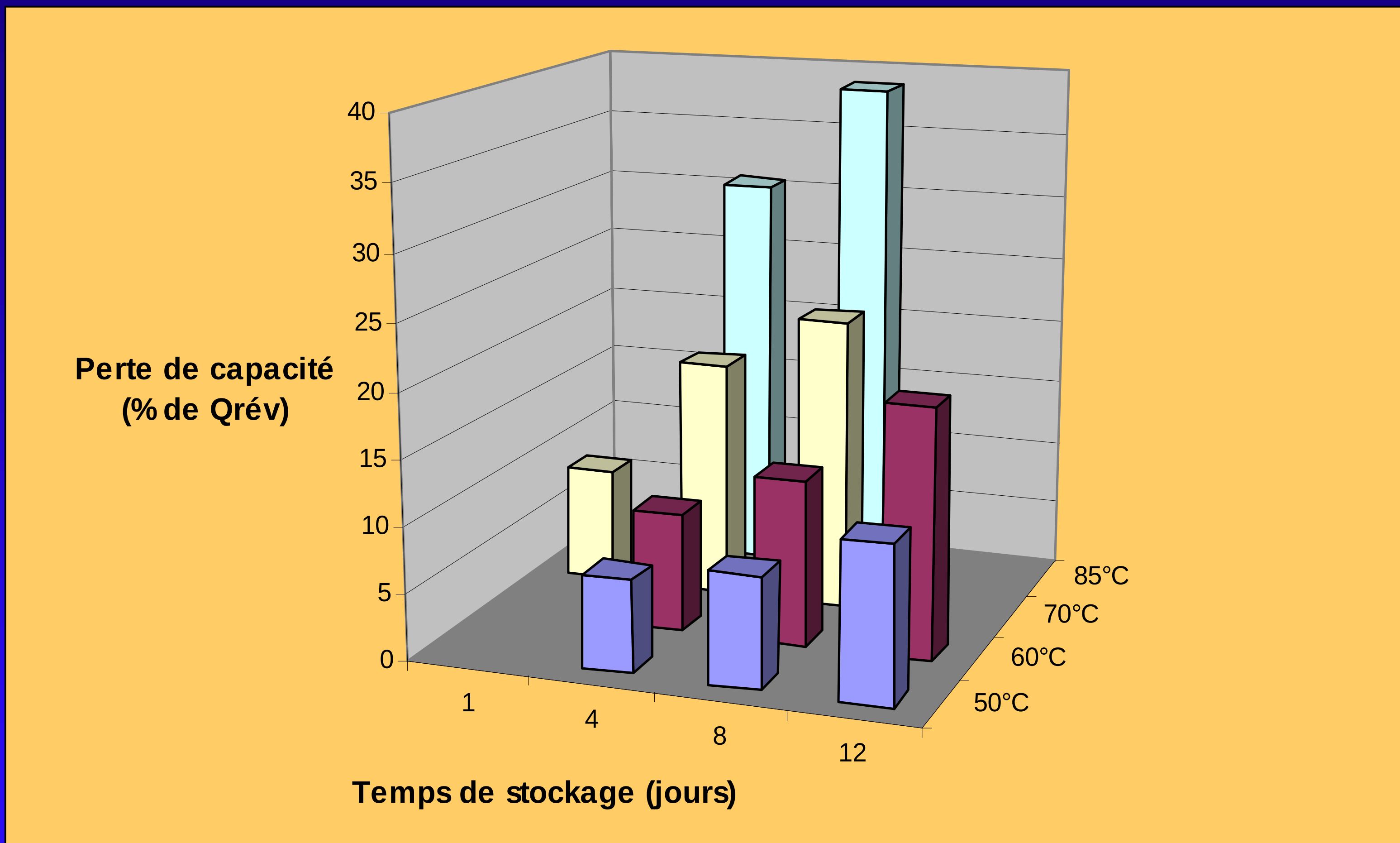
$$\approx k[Li_{ads}], car\ [Li_{ads}] << [Ox]$$

$$E = E^0 - \frac{RT}{F}\ln\left((1-x_\infty).e^{-kt} + x_\infty\right)$$

Activation energy (anodes)

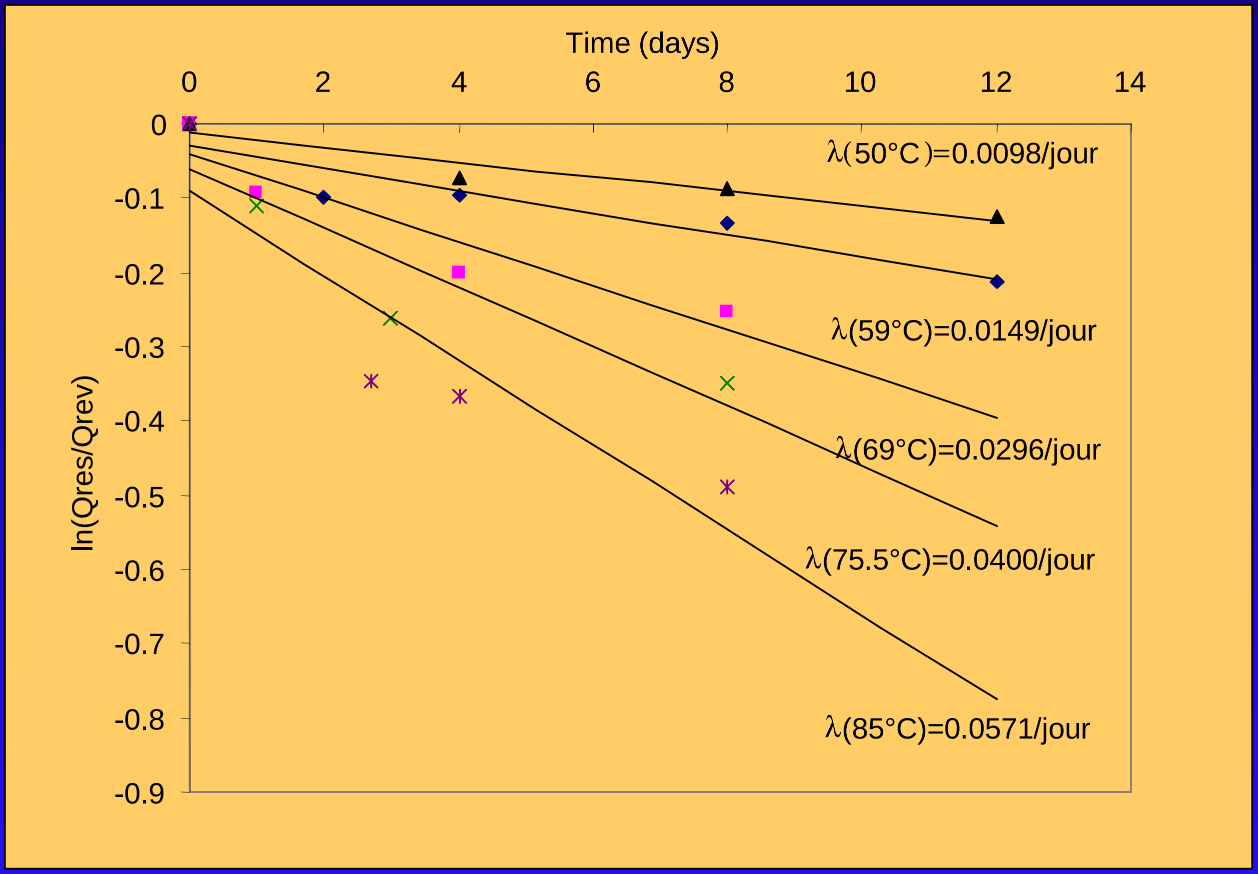


Capacity loss (anodes)



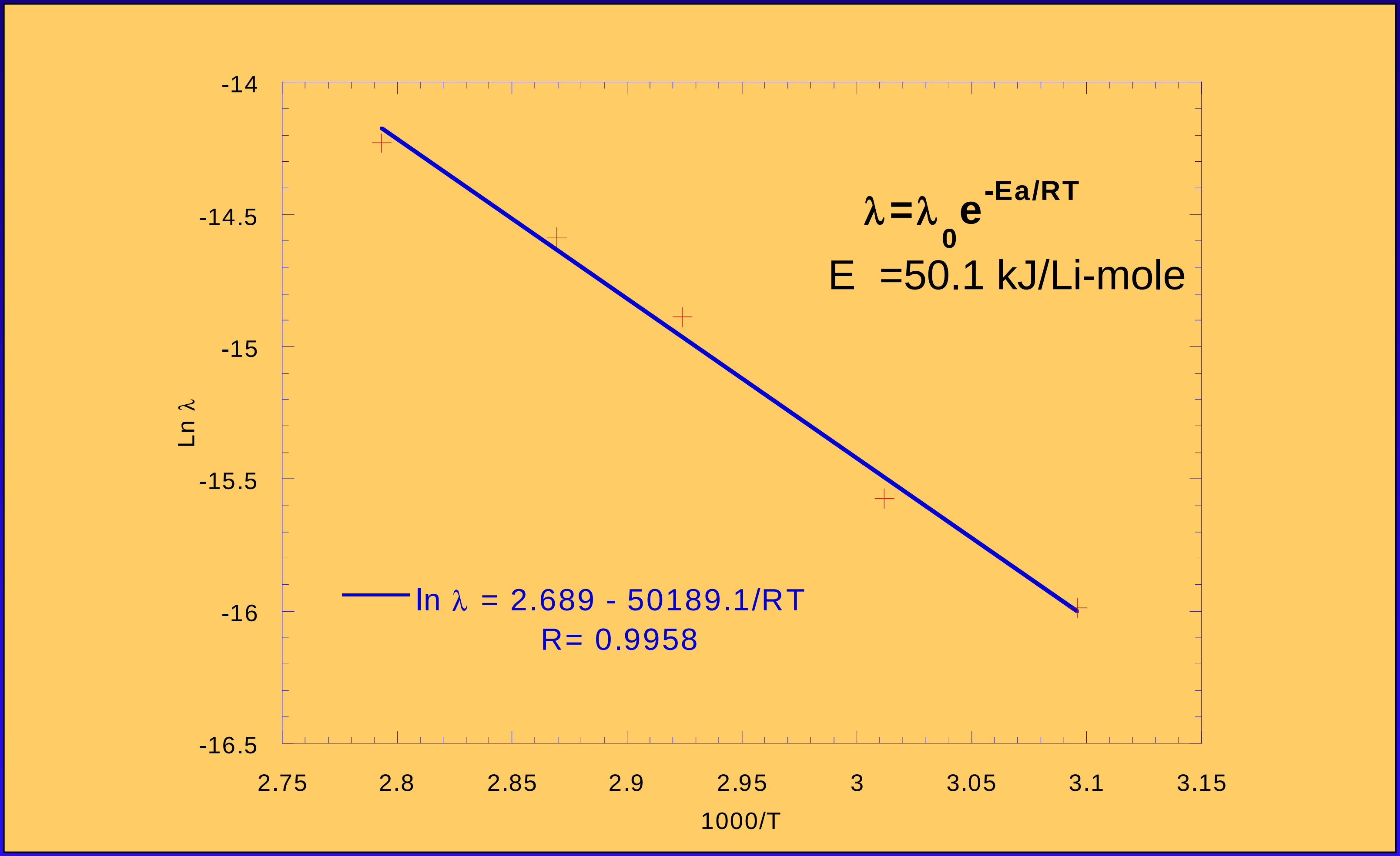
Kinetics of capacity loss (anodes)

$$Q_{residuelle} = Q_{reversible}.e^{-\lambda t}$$



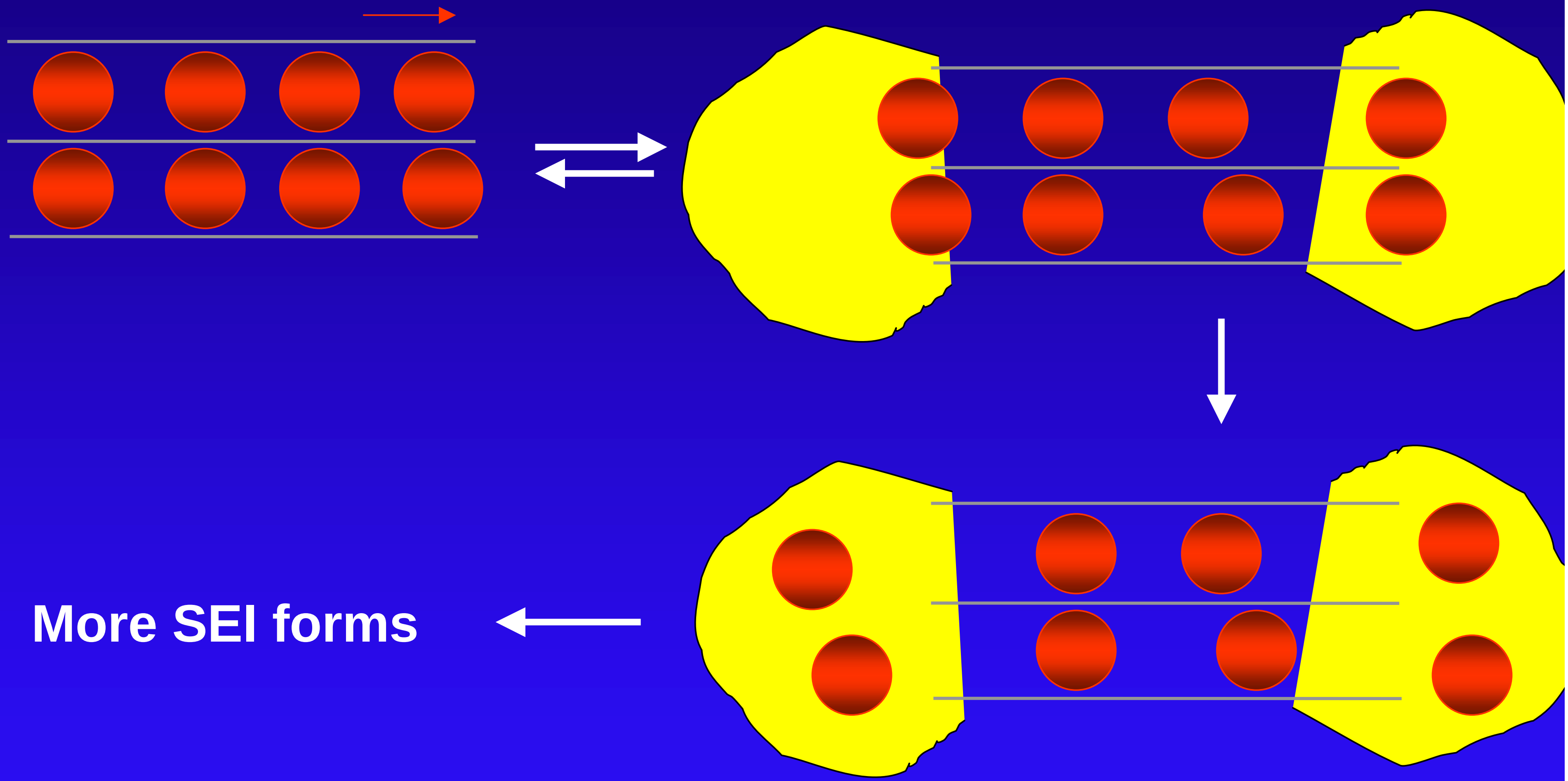
Kinetics of capacity loss (anodes)

Activation energy

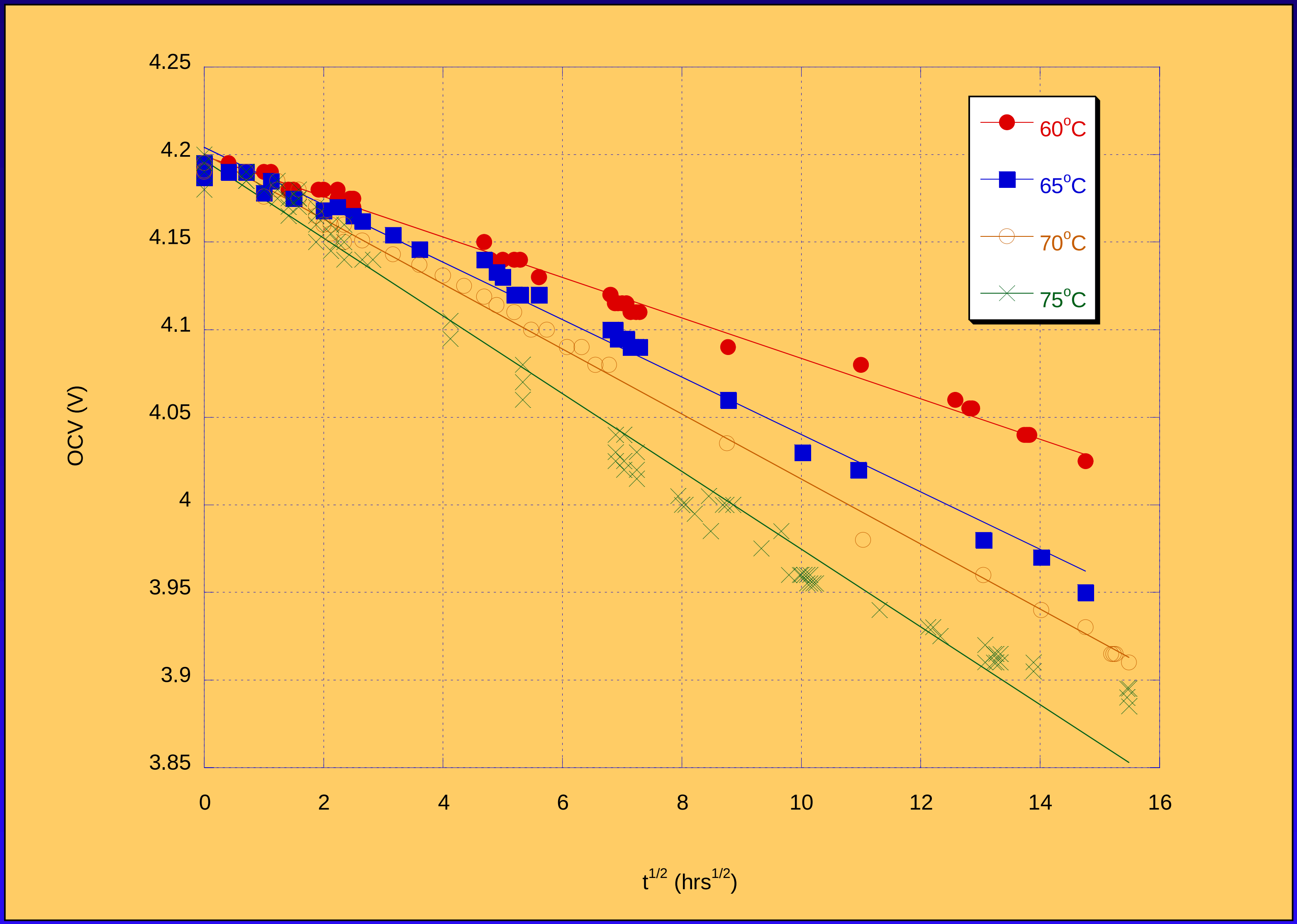


Mechanism of SD in graphite anodes (II

The (Li^+, e^-, molecule) adsorbed complex



OCV measurements (Cathodes)



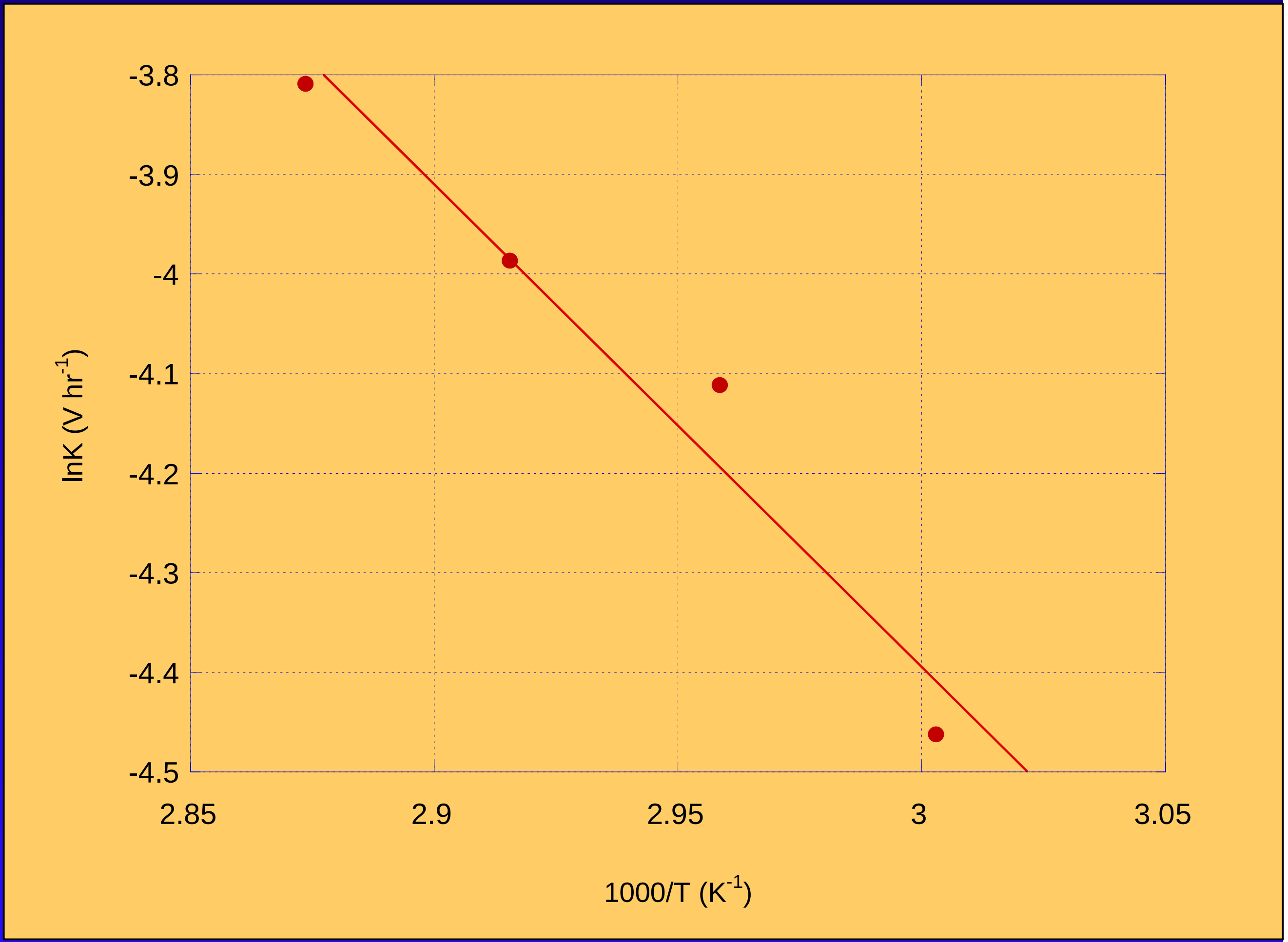
OCV measurements (Cathodes)

Kinetics and activation energy

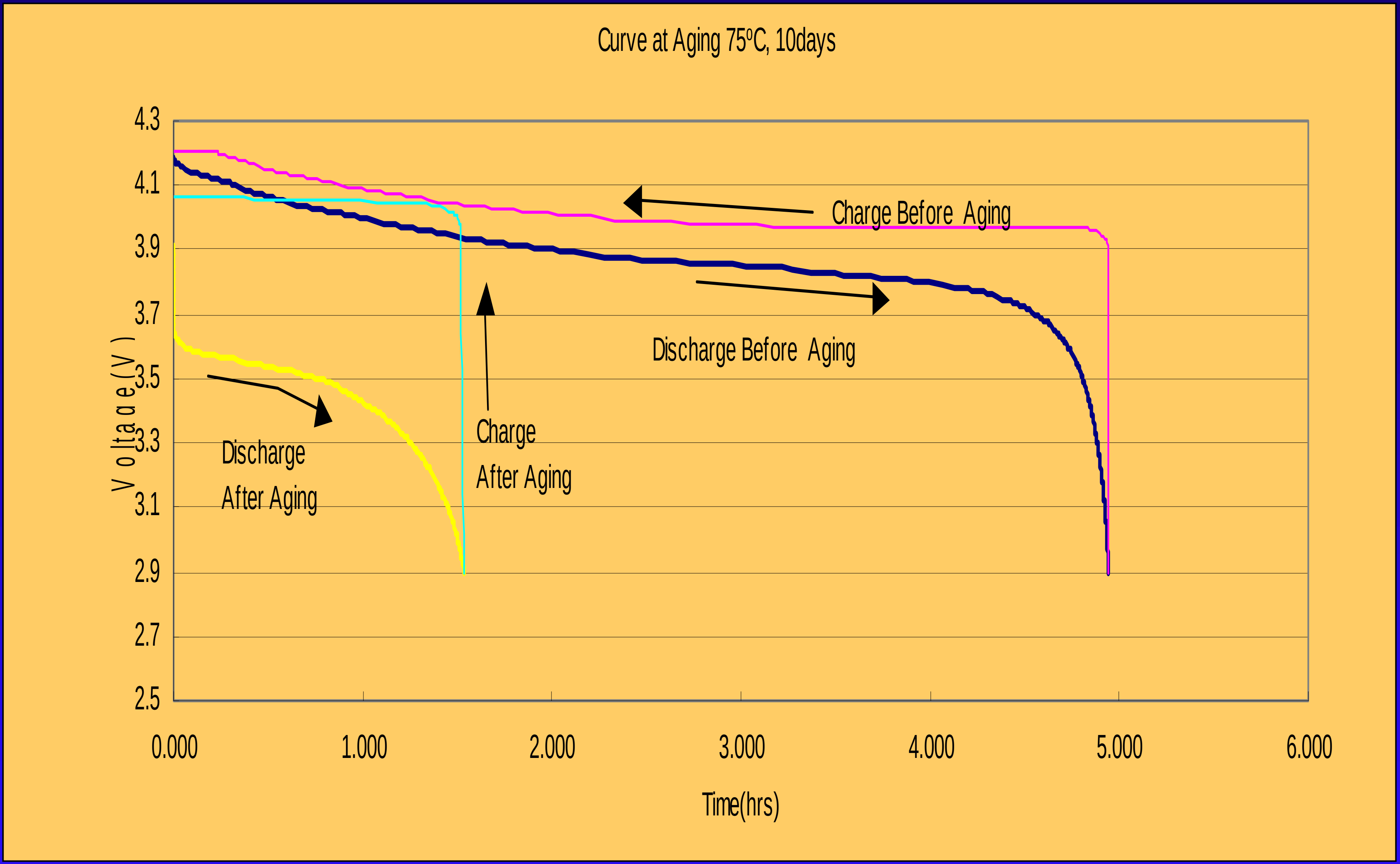
$OCV = OCV_0 - kt^{1/2}$

$k = k_0 \exp(-E_a/RT)$

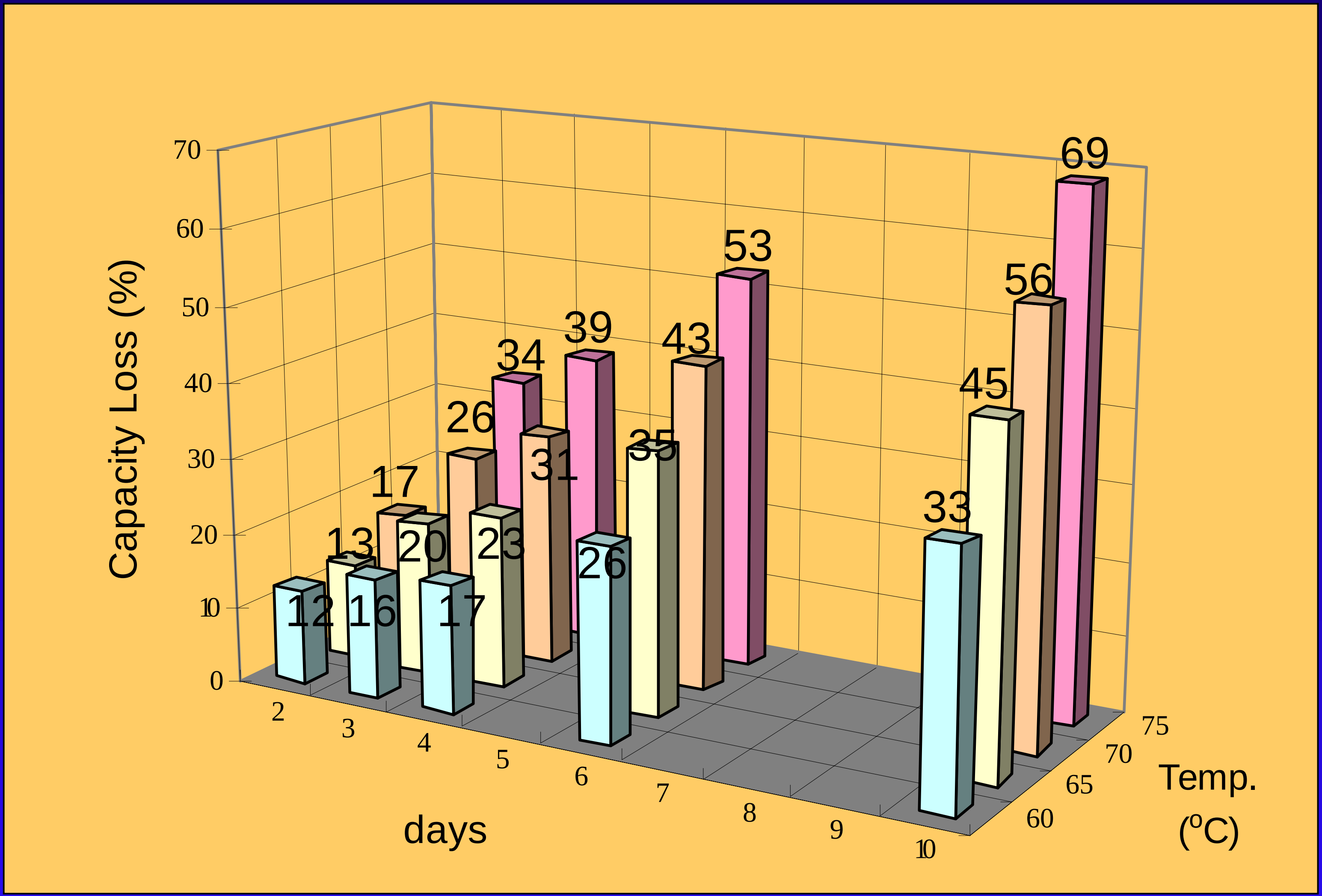
E_a = 41.3 kJ/Li-mole



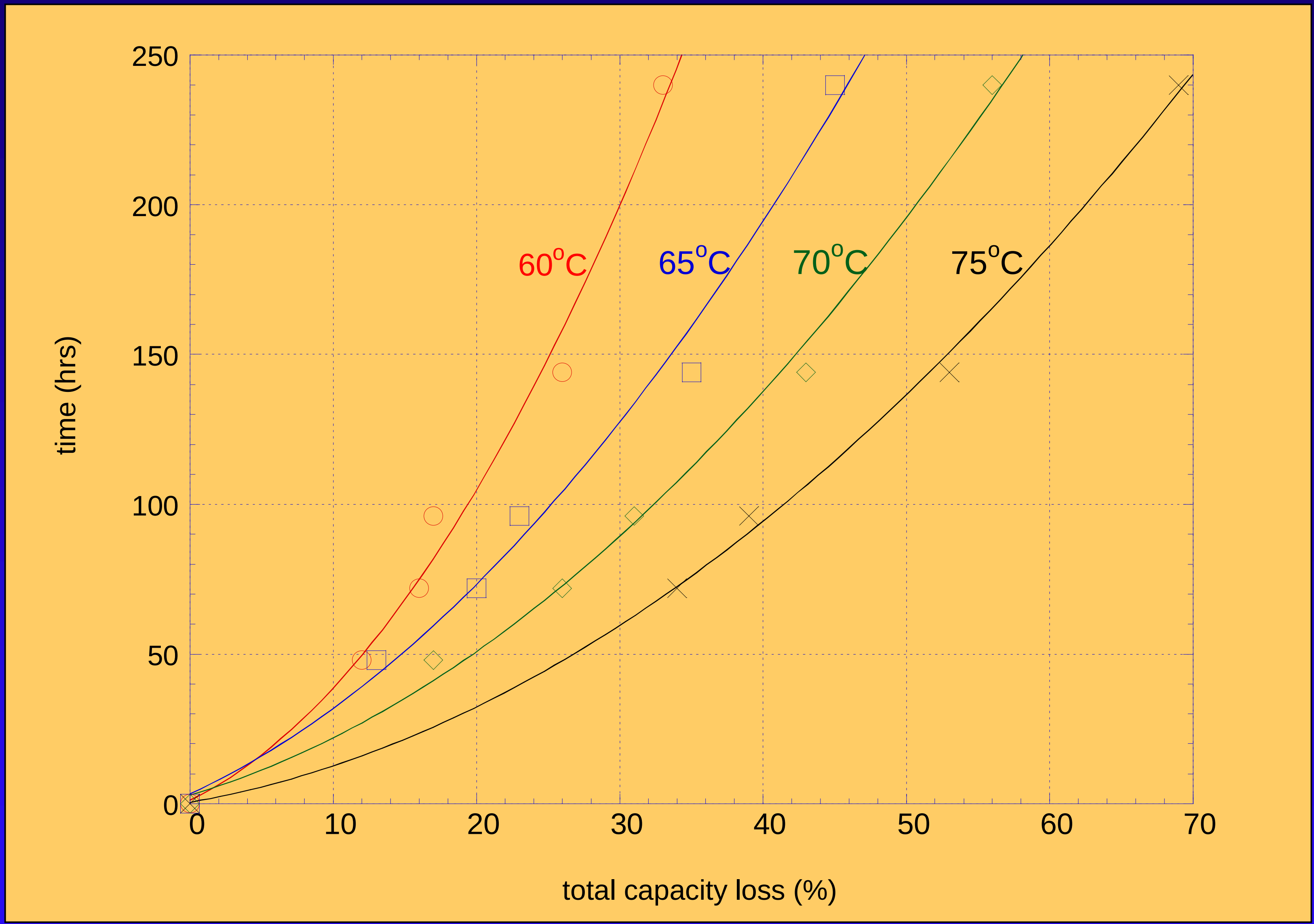
Aging Effect (Cathodes)



Total capacity loss (cathodes)

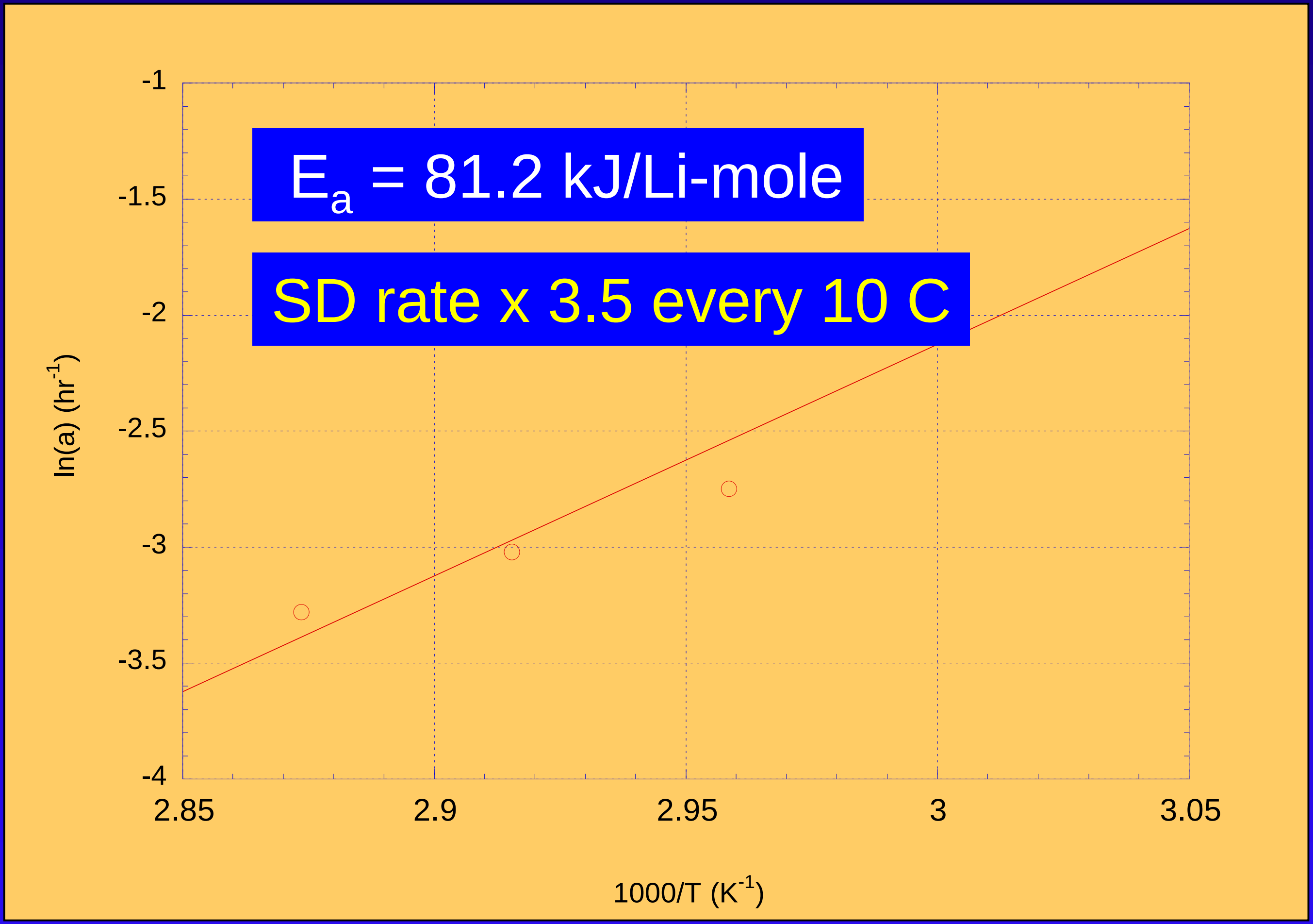


Kinetics law of SD (cathodes)

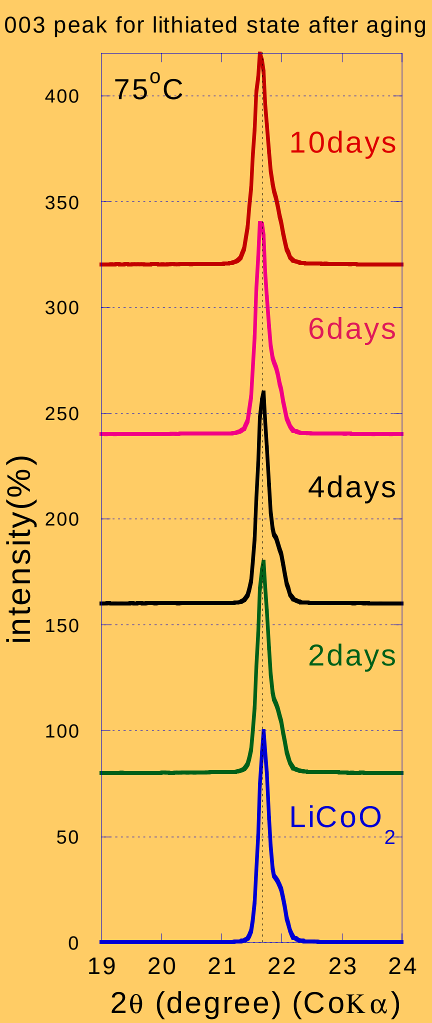


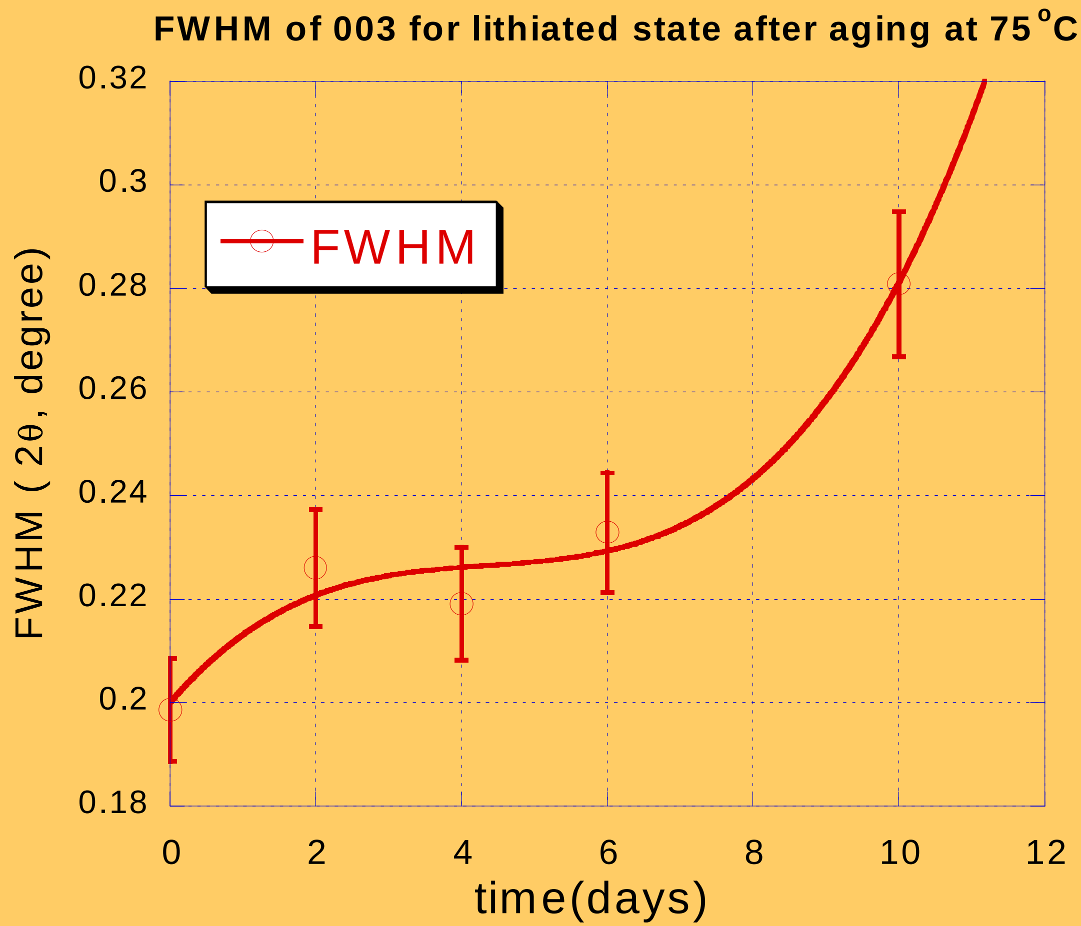
Kinetics law of SD (cathodes)

$$t = ax^2 + bx + c$$



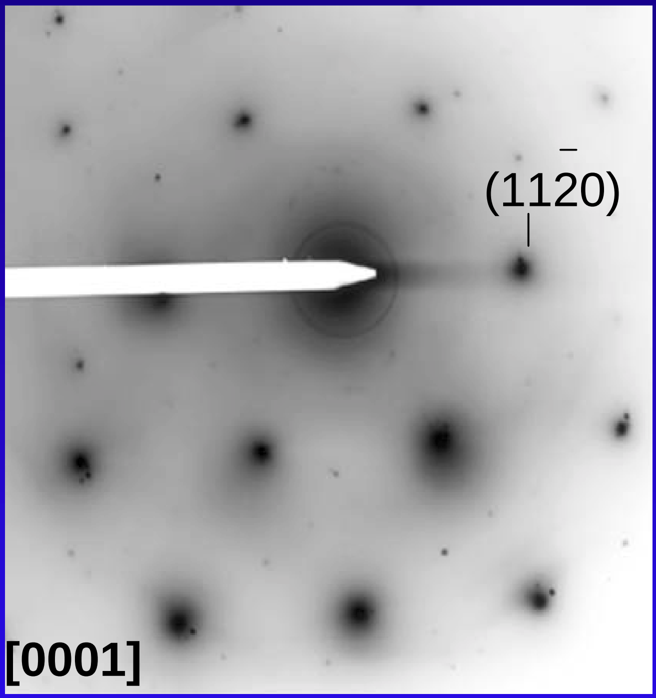
Mechanism of capacity loss: Structure changes



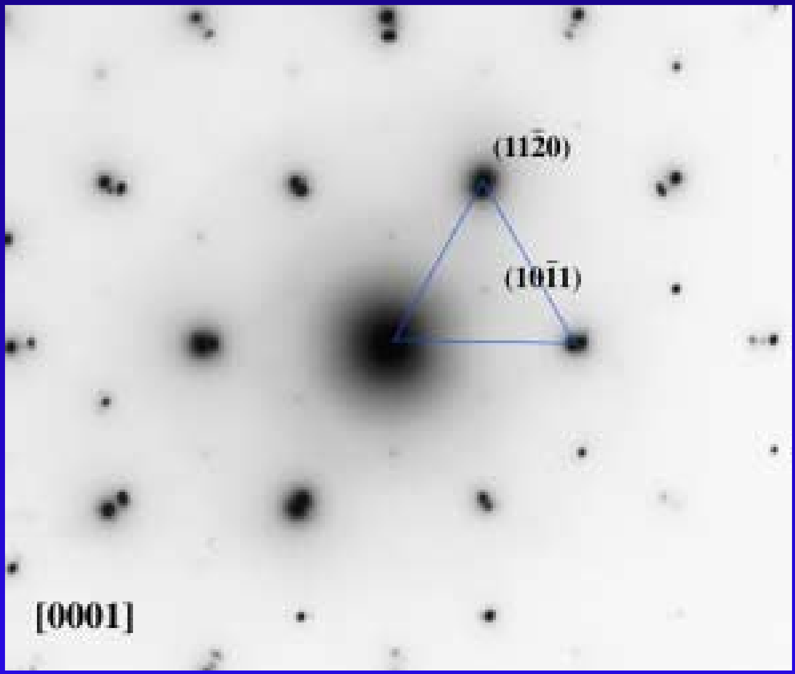


decrease crystallinity

LCO before and after aging

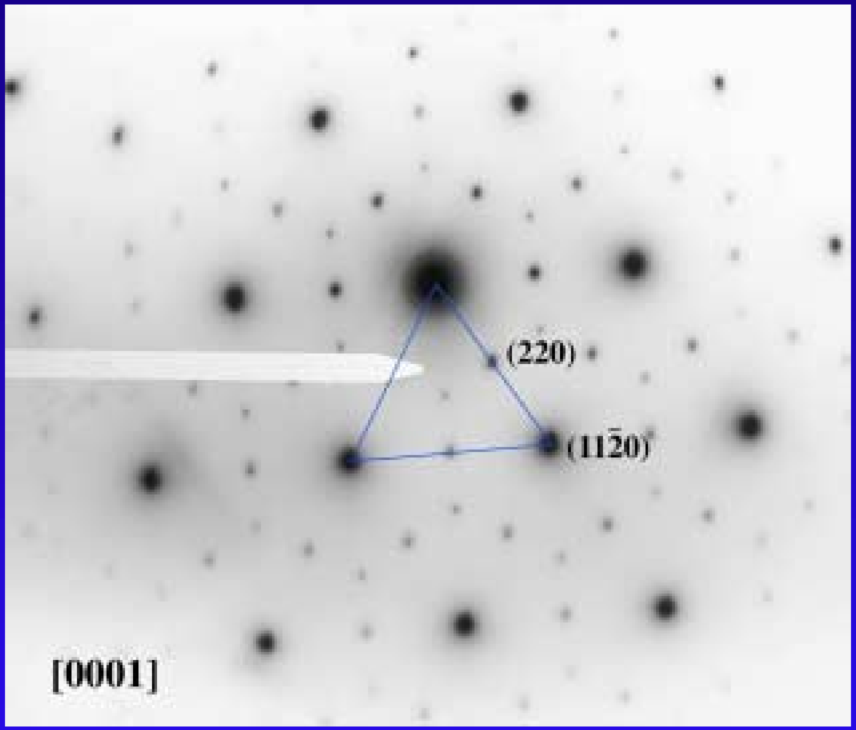


O3

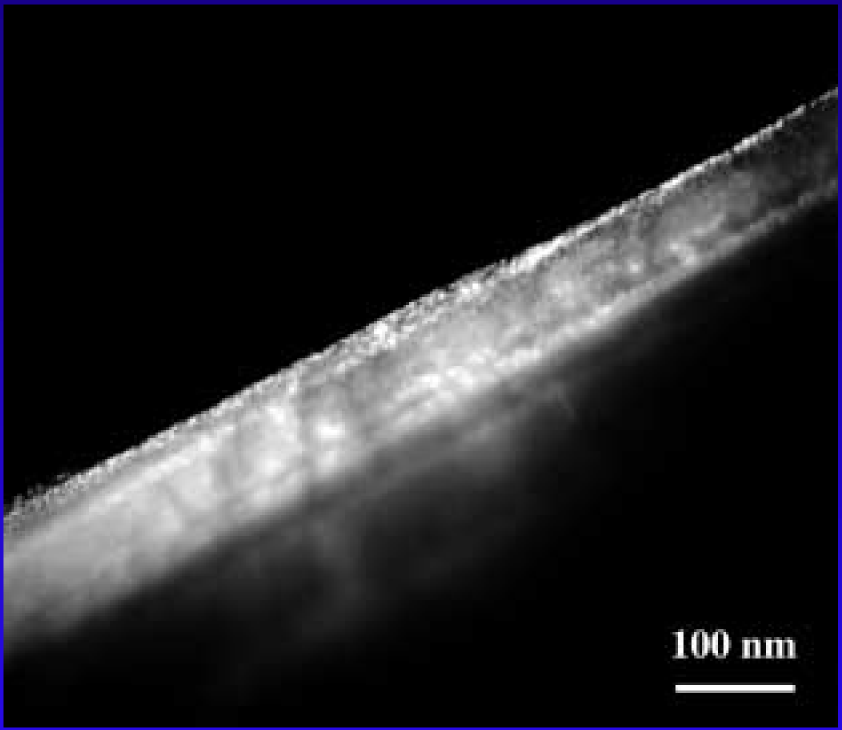


H1-3/O1 + spinel

Surface spinel

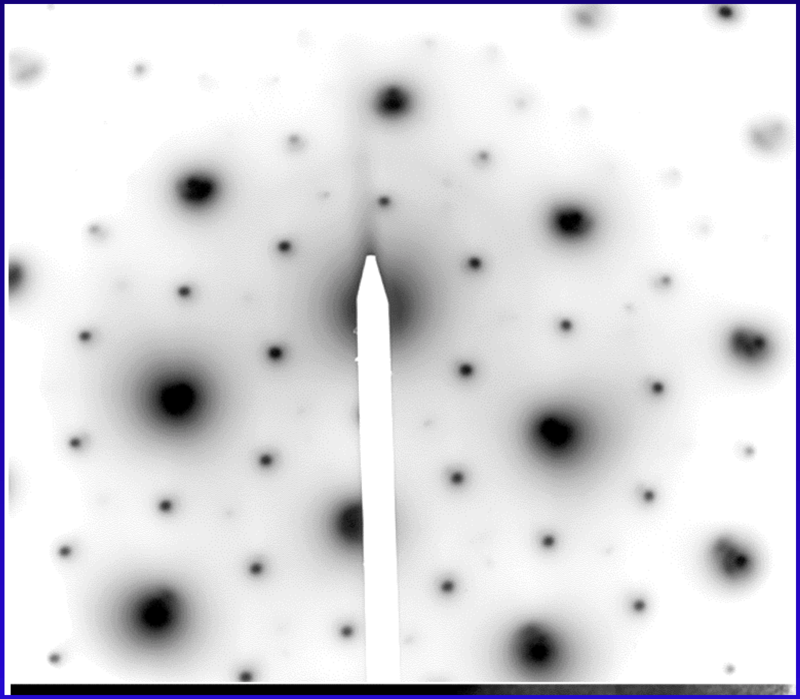


H1-3 + spinel



Dark field image

Heavily cycled LCO



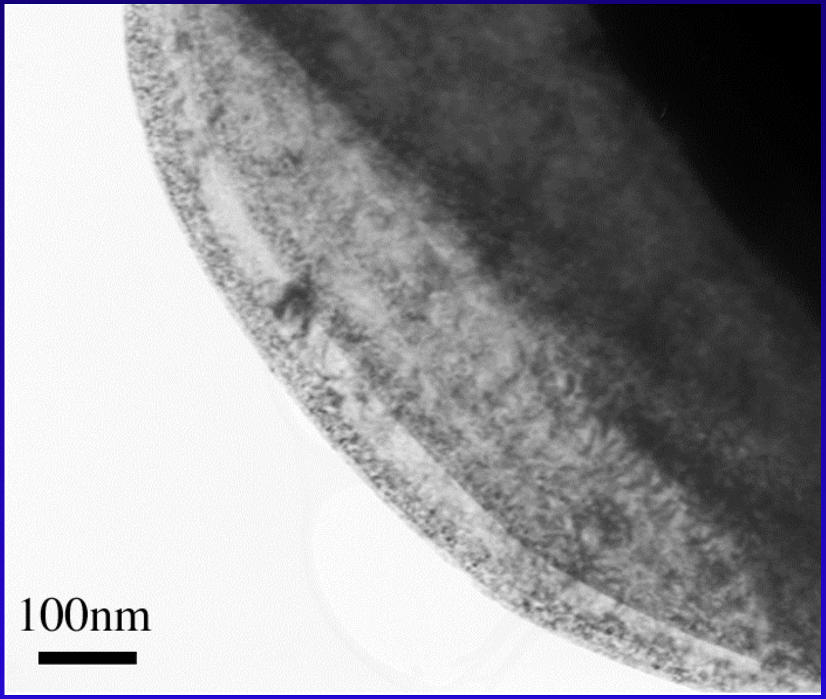
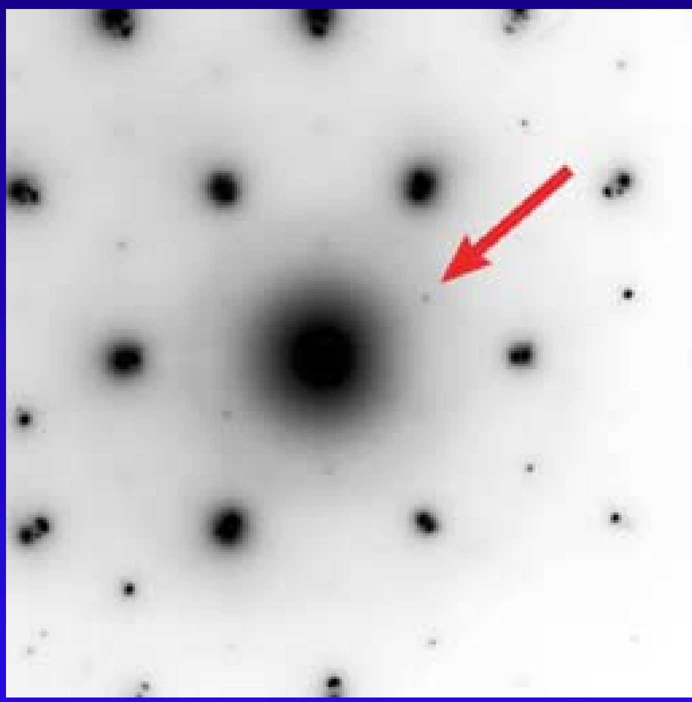


Image and Diffraction pattern after cycling (334x) at RT.
The SAD pattern shows extra spots corresponding to the structure of the cubic spinel.

The hexagonal to spinel phase transition

→ Irreversible capacity loss



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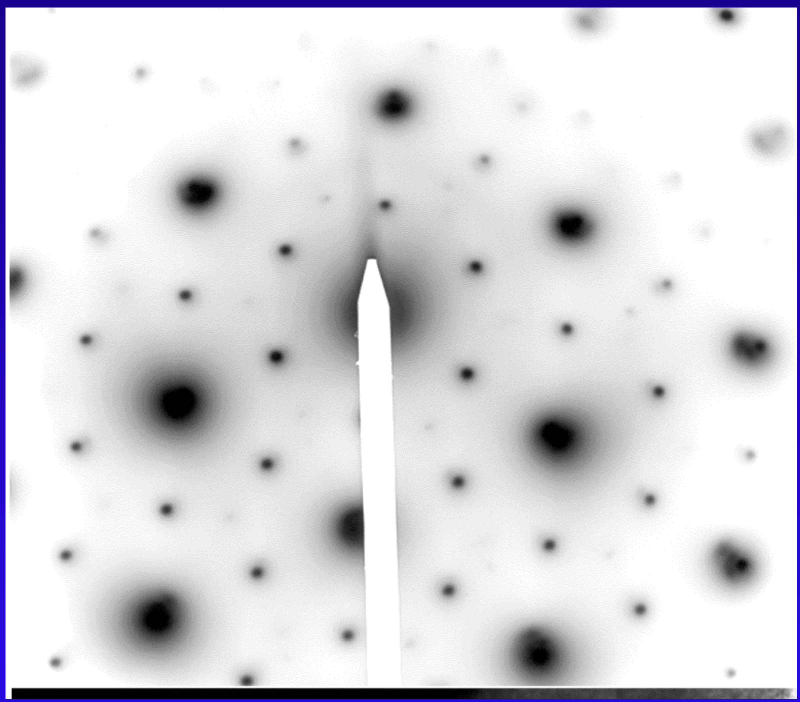


Hexagonal

Spinel

Abstract # 1119, poster session today

LIBs at Low Temperature

578 S. Herreyre et al. / Journal of Power Sources 97–98 (2001) 576–580

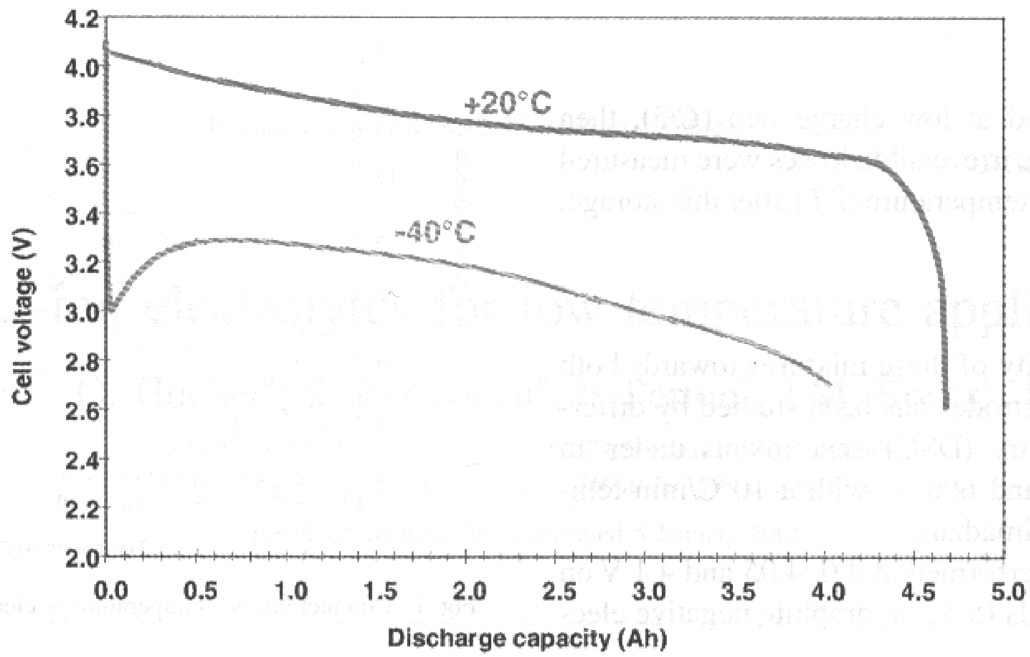
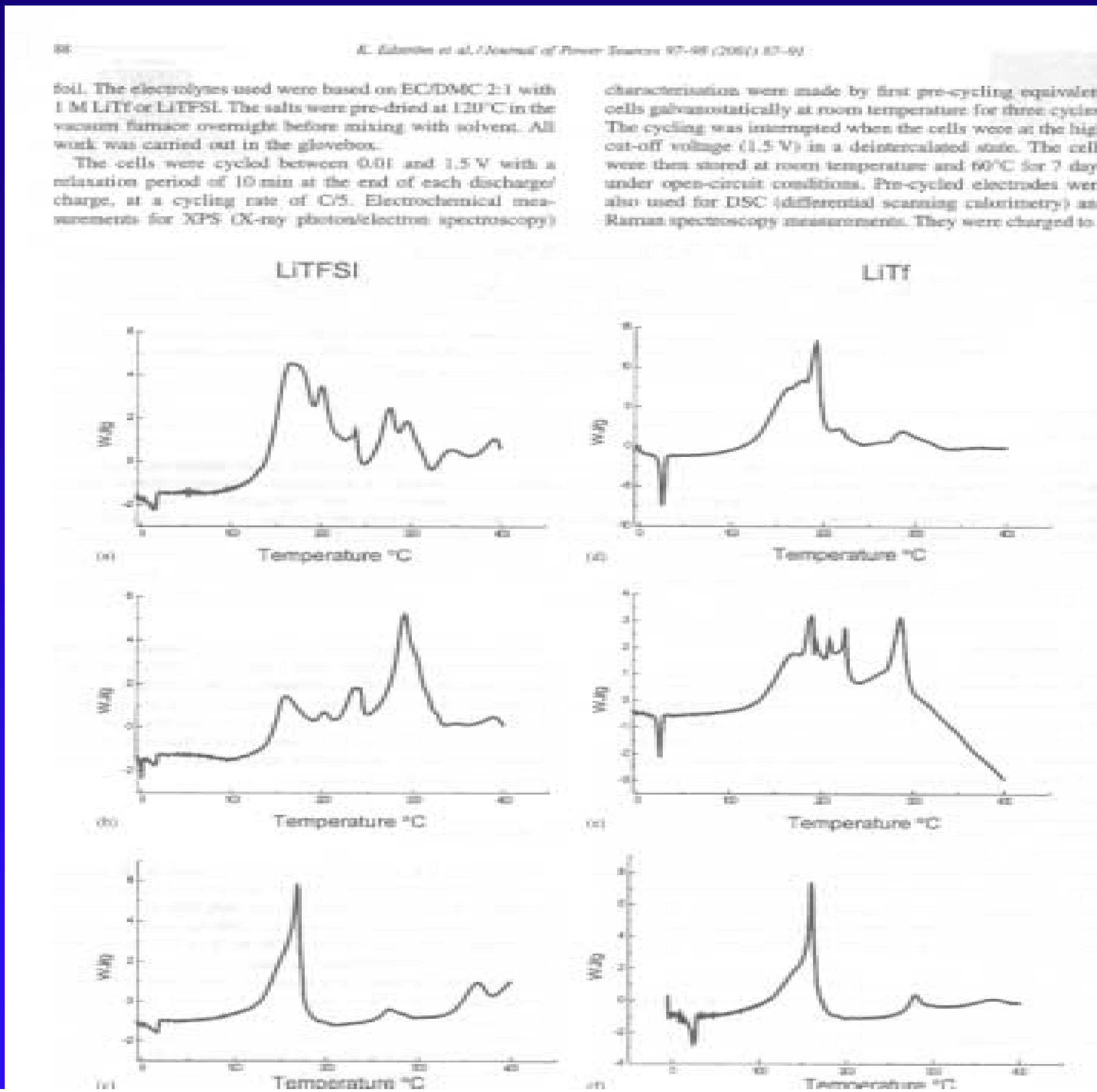


Fig. 2. Discharge characteristics in MP 174865 $LiCoO_2$||graphite cells. Electrolyte EC/DMC/EA $LiPF_6$ 1 M; charge 4.1 V at 4.6 A at RT; discharge at 0.92 A (*C*/5) at +20°C and −40°C.

The performances at LT are still to be improved

Abstract # 1119, poster session today

The components issues: 1) carbon anode



foil. The electrolytes used were based on EC/DMC 2:1 with 1 M LiTf or LiTFSI. The salts were pre-dried at 120°C in the vacuum furnace overnight before mixing with solvent. All work was carried out in the glovebox.

The cells were cycled between 0.01 and 1.5 V with a relaxation period of 10 min at the end of each discharge/charge, at a cycling rate of C/5. Electrochemical measurements for XPS (X-ray photon/electron spectroscopy) characterisation were made by first pre-cycling equivalent cells galvanostatically at room temperature for three cycles. The cycling was interrupted when the cells were at the high cut-off voltage (1.5 V) in a deintercalated state. The cells were then stored at room temperature and 60°C for 7 days under open-circuit conditions. Pre-cycled electrodes were also used for DSC (differential scanning calorimetry) and Raman spectroscopy measurements. They were charged to a

Two exothermic reactions:

- **150C: the SEI** reacts with electrolyte
- >250 C: lithium de-intercalates and reacts

The components issues: anode

Need for more stable LV ceramics Li-M-O anodes

Li-Ti-O :

• spinel phase $Li_4Ti_5O_{12}$

• ramsdellite phase: $Li_2Ti_3O_7$

Li-V-O or Li-W-O

• $LiVO_2$ and $LiWO_2$

Li-Fe-O such as $Li_6Fe_2O_3$

However: this will be at the expense of energy densit

The components issues: 2) cathode

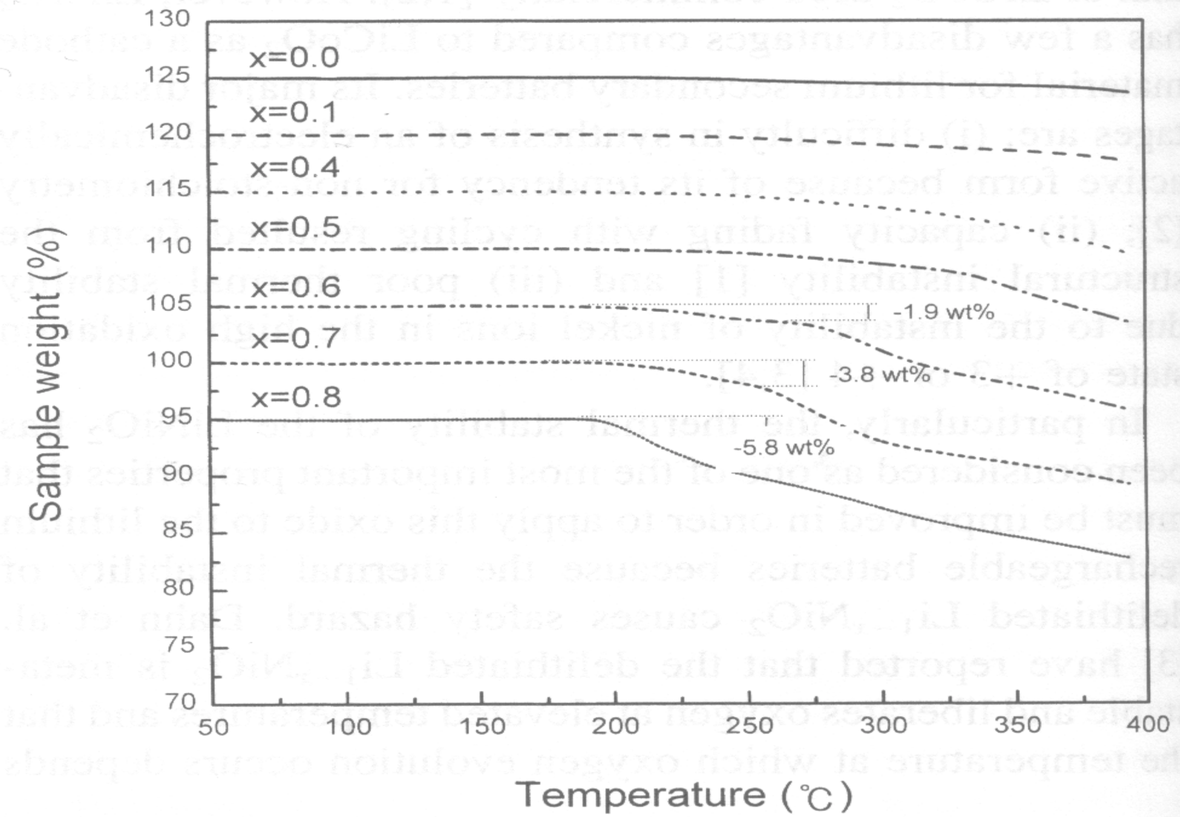
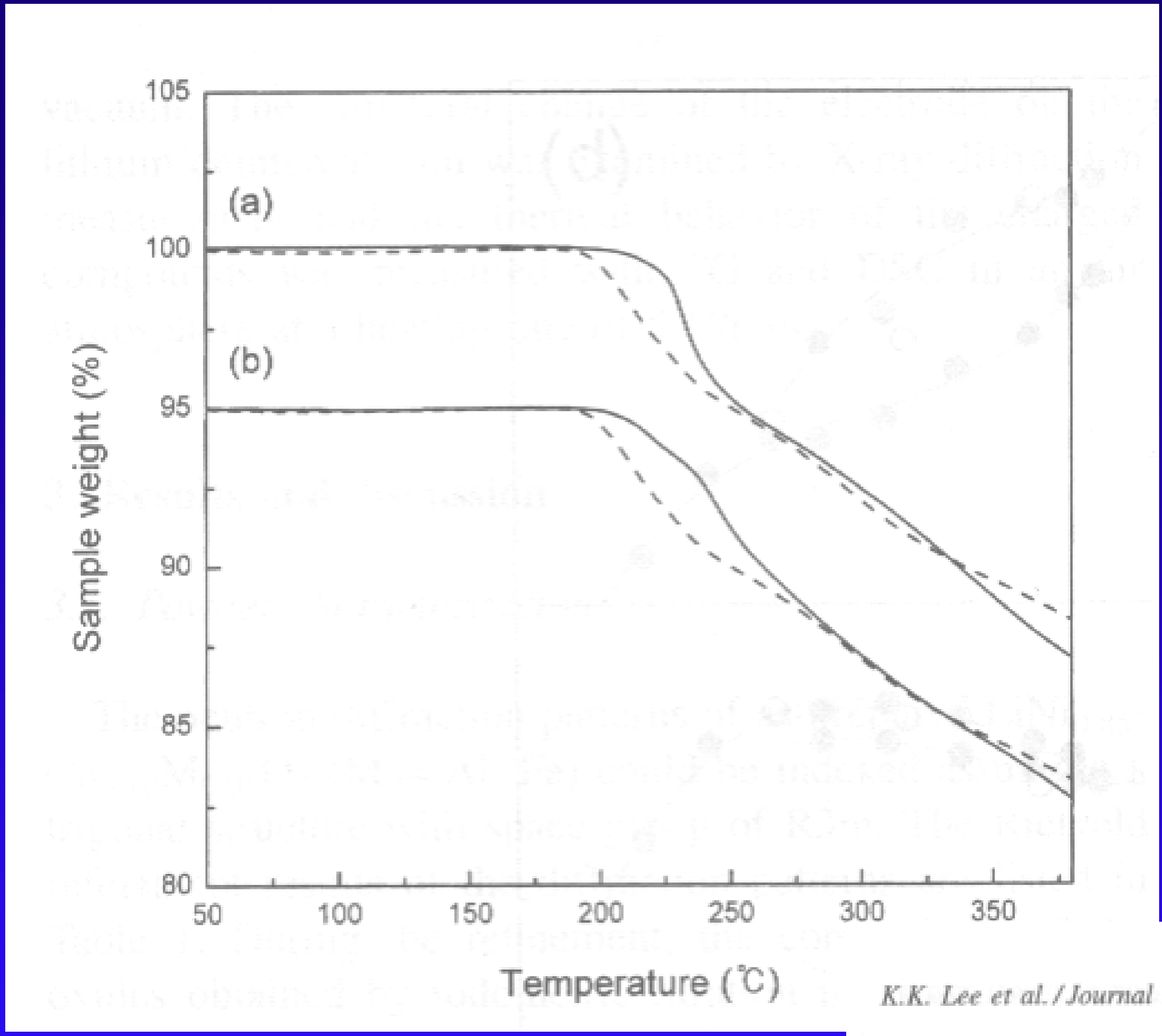


Fig. 1. TGA results for $Li_{1-x}NiO_2$ composites in an air atmosphere at a heating rate of 5°C/min. The data have been offset vertically by 5% sequentially for clarify.

K.-K. Lee et al. / Journal of Power Sources 97–98 (2001) 321–325

2) cathode: TMO (Co, Ni) +Al or Fe doping



K.K. Lee et al. / Journal of Power Sources 97–98 (2001) 308–31

Olivine-Type Cathodes for Lithium-ion Batteries
$Li^{+}M^{2+}(PO_4)^{3-}$ (M=Transition Metals)

$$LiM^{2+}PO_4 \longleftrightarrow M^{3+}PO_4 + Li^{+} + e^{-}$$

1. The presence of **$(PO_4)^{3-}$ polyanion**
2. The use of **M^{3+}/M^{2+} redox reaction**

↓

Stable operation at high voltage

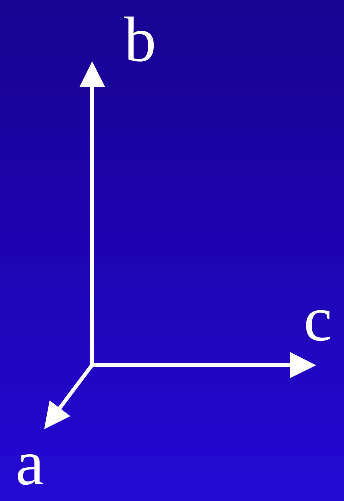
3.4V: Fe^{3+}/Fe^{2+}

4.1V: Mn^{3+}/Mn^{2+}

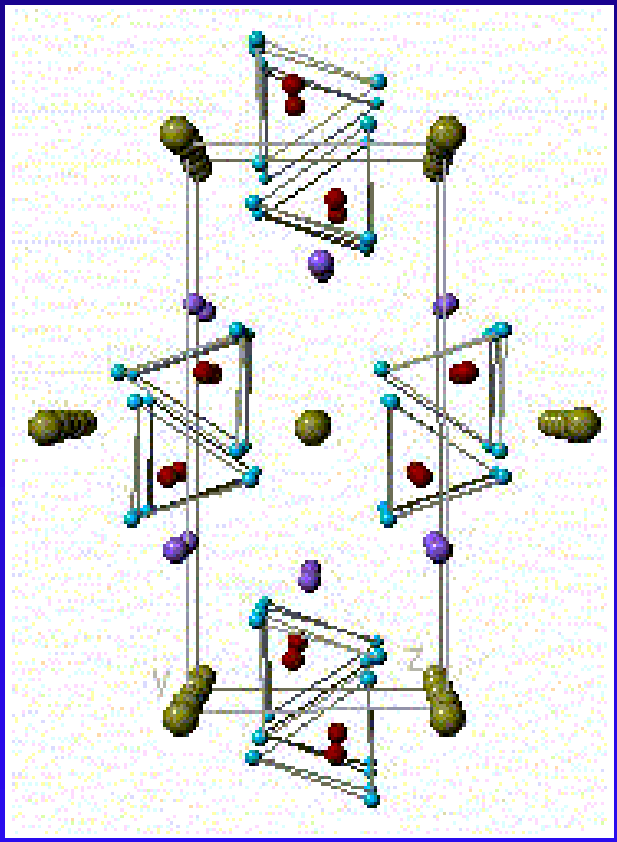
4.8V: Co^{3+}/Co^{2+}

Crystal Structure of Ordered-Olivines

Orthorhombic / D_{2h}^{16} - Pmnb

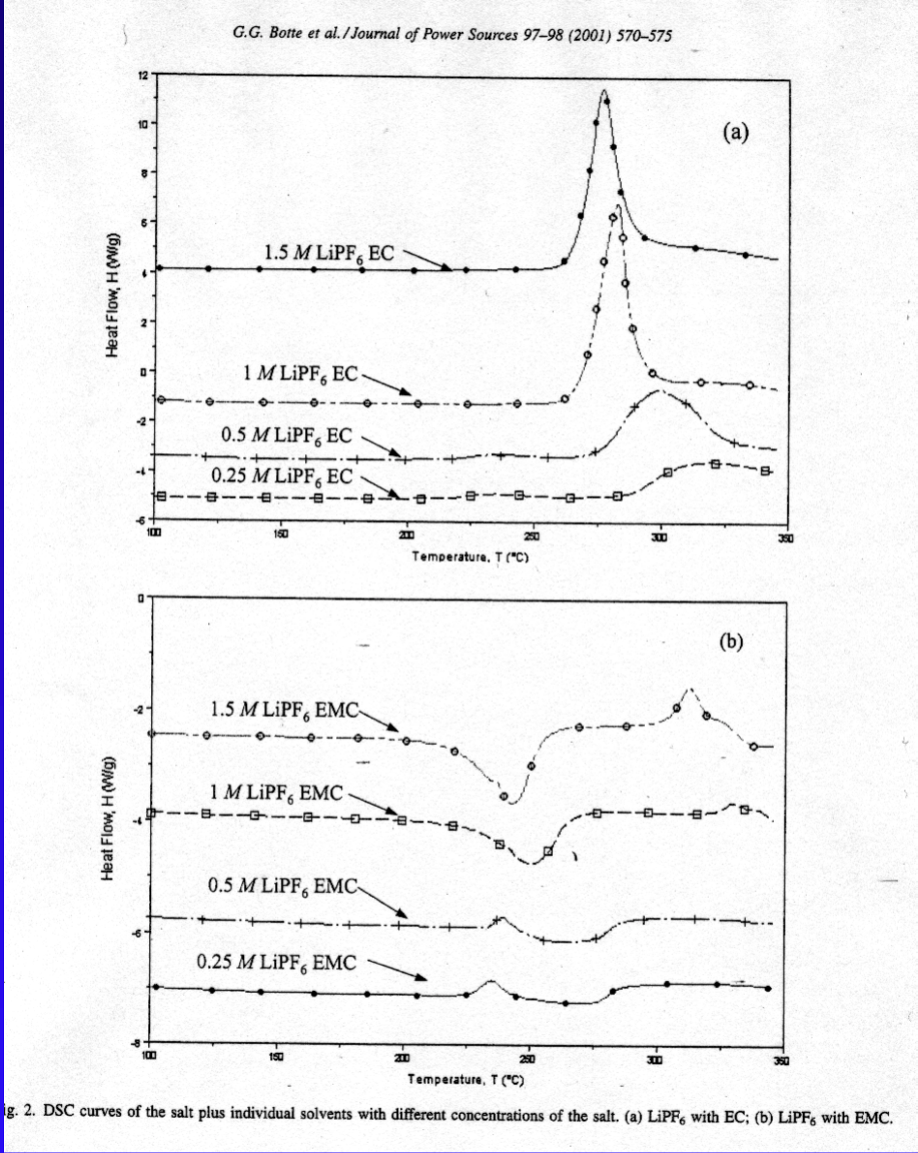


a = 6.008(1) Å
b = 10.324(2) Å
c = 4.750(2) Å



$LiFePO_4$

The components issues: 3) electrolyte



The components issues: 3) electrolyte

Table 1
Summary of the onset temperatures and heat of reactions of the results shown in Figs. 1–3[a]

Material	$T_i \pm 1$°C	$T_f \pm 1$°C	$T_{onset} \pm 1$°C	H_R (J/g)[b]
$LiPF_6$	180	210	194	20 ± 2
EC	205	250	211	−23 ± 2
EMC	195	230	205	−10 ± 1
DEC:DMC (1:1)	200	245	208	−22 ± 2
EC:EMC (1:1)	205	250	209	−11 ± 1
EC:DEC:DMC (1:1:1)	195	235	205	−20 ± 2
1 M $LiPF_6$–EC	250	>350	270	>−620 ± 60
1 M $LiPF_6$–EMC	195	280	233	160 ± 20
	320	340	324	−22 ± 2
1 M $LiPF_6$–DEC:DMC (1:1)	195	280	231	150 ± 20
1 M $LiPF_6$–EC:EMC (1:1)	200	250	228	30 ± 3
	250	>350	253	>−330 ± 30
1 M $LiPF_6$–EC:DEC:DMC (1:1:1)	200	250	225	76 ± 8
	250	>350	256	>210 ± 20
0.25 M $LiPF_6$–EC	200	261	219	−21 ± 2
	280	>350	290	>−170 ± 20
0.5 M $LiPF_6$–EC	207	260	219	−21 ± 2
	263	>350	277	>−500 ± 50
1.5 M $LiPF_6$–EC	244	>350	267	>−740 ± 70
0.25 M $LiPF_6$–EMC	213	244	227	−15 ± 1
	244	290	No define	38 ± 4
0.5 M $LiPF_6$–EMC	226	246	234	−9 ± 1
	246	288	No define	44 ± 4
1.5 M $LiPF_6$–EMC	186	267	228	180 ± 20
	285	330	304	−43 ± 4
0.25 M $LiPF_6$–EC:EMC (1:1)	275	>350	312	>−84 ± 8
0.5 M $LiPF_6$–EC:EMC (1:1)	240	>350	261	>−260 ± 30
1.5 M $LiPF_6$–EC:EMC (1:1)	200	250	225	40 ± 4
	250	>350	248	>−320 ± 30
2 M $LiPF_6$–EC:EMC (1:1)	200	250	219	41 ± 4
	250	>350	240	>−340 ± 30
1 M $LiPF_6$–EC:EMC (1:2)	180	250	225	51 ± 5
	250	>350	255	>−260 ± 30
1 M $LiPF_6$–EC:EMC (2:1)	180	250	225	15 ± 2
	250	>350	250	>−340 ± 30

[a] T_i, T_f, T_{onset}, and H_R represent the initial decomposition temperature, the final decomposition temperature, the onset temperature and the heat of reaction, respectively.
[b] Negative values indicate exothermic reaction.

More thermally stable electrolytes are needed

Hybrid electrolytes:

gels: polymer + liquid
polymers in salts
LT molten salts
Glass-type electrolytes

- The LT conductivity may be a problem!
- Interfacial impedance should be optimized
- Adapted separators are needed with new safety features (glass fibers, ceramics,..)

Li/CF$_x$ primary batteries operating Between -40 and 150 C

COIN TYPE-HIGH TEMPERATURE

Model Number	Dimensions (mm) D	Dimensions (mm) T	Nominal Voltage (V)	Nominal Capacity (mAh)	Temp. Range °C
BR1225A*	12.5	2.5	3	48	-40° C~150° C
BR1632A	16.0	3.2	3	120	-40° C~150° C
BR2330A	23.0	3.0	3	255	-40° C~150° C
BR2477A	24.5	7.0	3	1000	-40° C~125° C

* Under development

Sealing technology: metal-ceramics seals (Matsushita's patent)

CONCLUSION

Today's LIB is not viable for extreme environments

R&D efforts should be undertaken to find highly stable chemistries including new anodes, cathodes and electrolytes. Some have already been explored but not extensively enough

Due to wide temperature and pressure ranges, the new chemistries may make it necessary to compromise the energy density and/or cycle life.

Primary Li batteries are also an alternative, provided low temperature electrolytes are found.

Basic research is still needed to understand the electrochemically active and inactive materials behavior under extreme environments such as at low and high temperatures and high pressure.